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ON
INORGANIC AND THEORETICAL CHEMISTRY

BY

J. W. MELLOR, D.Sc., F.R.S.

VOLUME X

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TO THE

PRIVATES IN THE GREAT ARMY
OF WORKERS IN CHEMISTRY

THEIR NAMES HAVE BEEN FORGOTTEN

THEIR WORK REMAINS

2881K

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ABBREVIATIONS

aq. = aqueous
atm. = atmospheric or atmosphere(s)
at. vol. = atomic volume(s)
at. wt. = atomic weight(s)
T° or °K = absolute degrees of temperature
b.p. = boiling point(s)
θ° = centigrade degrees of temperature
coeff. = coefficient
conc. = concentrated or concentration
dil. = dilute
eq. = equivalent(s)
f.p. = freezing point(s)
m.p. = melting point(s)
mol(s) = $\left\{\begin{array}{l}\text{gram-molecule(s)}\\ \text{gram-molecular}\end{array}\right.$
mol(s). = $\left\{\begin{array}{l}\text{molecule(s)}\\ \text{molecular}\end{array}\right.$
mol. ht. = molecular heat(s)
mol. vol. = molecular volume(s)
mol. wt. = molecular weight(s)
press. = pressure(s)
sat. = saturated
soln. = solution(s)
sp. gr. = specific gravity (gravities)
sp. ht. = specific heat(s)
sp. vol. = specific volume(s)
temp. = temperature(s)
vap. = vapour

In the **cross references** the first number in clarendon type is the number of the volume; the second number refers to the chapter; and the succeeding number refers to the "§," section. Thus **5.** 38, 24 refers to § 24, chapter 38, volume 5.

The oxides, hydrides, halides, sulphides, sulphates, carbonates, nitrates, and phosphates are considered with the basic elements; the other compounds are taken in connection with the acidic element. The double or complex salts in connection with a given element include those associated with elements previously discussed. The carbides, silicides, titanides, phosphides, arsenides, etc., are considered in connection with carbon, silicon, titanium, etc. The intermetallic compounds of a given element include those associated with elements previously considered.

The use of **triangular diagrams** for representing the properties of three-component systems was suggested by G. G. Stokes (*Proc. Roy. Soc.*, **49**. 174, 1891). The method was immediately taken up in many directions and it has proved of great value. With practice it becomes as useful for representing the properties of ternary mixtures as squared paper is for binary mixtures. The principle of triangular diagrams is based on the fact that in an equilateral triangle the sum of the perpendicular distances of any point from the three sides is a constant. Given any three substances *A*, *B*, and *C*, the composition of any possible combination of these can be represented by a point in or on the triangle. The apices of the triangle represent the single components *A*, *B*, and *C*, the sides of the triangle represent binary mixtures of *A* and *B*, *B* and *C*, or *C* and *A*; and points within the triangle, ternary mixtures. The compositions of the mixtures can be represented in percentages, or referred to unity, 10, etc. In Fig. 1, pure *A* will be represented by a point at the apex marked *A*. If 100 be the standard of reference, the point *A* represents 100 per cent. of *A* and nothing else; mixtures containing 80 per cent. of *A* are represented by a point on the line 88, 60 per cent. of *A* by a point on the line 66, etc. Similarly with *B* and *C*—Figs. 3 and 2 respectively. Combine Figs. 1, 2, and 3 into one diagram by superposition, and Fig. 4 results. Any point in this diagram, Fig. 4, thus represents a ternary mixture. For instance, the point *M* represents a mixture containing 20 per cent. of *A*, 20 per cent. of *B*, and 60 per cent. of *C*.

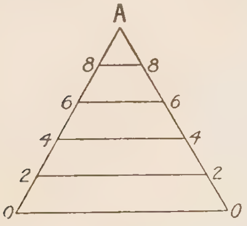
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Fig. 1.

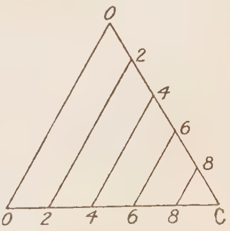
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Fig. 2.

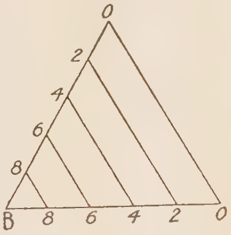
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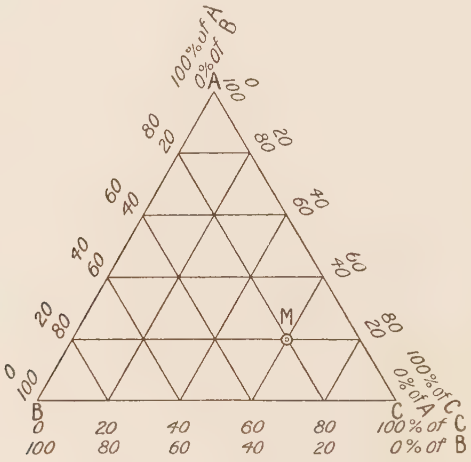
Fig. 3.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0
100
100% of C
0% of A
M
B
C
0
20
40
60
80
100% of C
100
80
60
40
20
0% of B

Fig. 4.—Standard Reference. Triangle.

CHAPTER LVII

SULPHUR

§ 1. The History of Sulphur

Sulphur has been known from very early times. It is called *Schwefel* in Germany; *soufre* in France; *solfo* or *zolfo* in Italy; *zufre* or *azufre* in Spain; and *svafvel* in Sweden. The name is said to be derived from the Sanscrit *sulvere* through the Latin *sulphurium* or *sulphurum*. Isodorus' suggestion that that term is a corruption of *sal πῦρ*, is not accepted. Sulphur was then frequently called *lapis ardens*. The vernacular name of sulphur was formerly *brimstone*, and that term is still used when referring to its inflammable character –*e.g.* it is often mentioned in the Bible, *Revelation* (**19**. 20), etc. In the Pentateuch—*Genesis*, **19**. 24—cities were destroyed *πυρὶ καὶ θεῖω*—by fire and brimstone. Ancient writers frequently mention a sulphurous smell accompanying lightning, and it has been suggested that the Greek term *θεῖον*, divine, was extended to sulphur, for sulphur then appeared to accompany divine manifestations. The term *θεῖον* is frequently used by Homer for sulphur—*e.g.* in the *Odyssea* (**22**. 481), where, after the slaughter of the suitors, Odysseus, recognizing the need for a general clean-up, called: "Quickly, O! Dame, bring fire that I may burn sulphur, the cure of ills"—and sulphur was then used as a fumigating agent, for Homer also speaks of the "pest-averting sulphur," the "divine and purifying fumigation," etc. Sulphur was also used by the ancients in some of their religious ceremonies; indeed, the very term is itself derived from *θεός*, meaning God. Dioscorides, in his *Περὶ γλής Ἰατρικῆς*, written in the first century of our era, referred to *ἄπυρον θεῖον*, meaning pure or native sulphur, and to *πεπυρωμένον θεῖον*, meaning sulphur extracted by means of fire. There are several allusions to sulphur in contemporaneous writers. Thus, Juvenal, in his *Satiræ* (**4**. 46–47); Martial, in his *Epigrammata* (**1**. 42; **10**. 3); Ovid, in his *Fasti* (**4**. 739), referred to "cleaning and purifying sulphur," and, in his *Ars amatoria* (**2**. 330), he alluded to the purification of houses with eggs and sulphur; and Apuleius, in his *Metamorphoses* (**11**. 16), mentioned a purification by a priest of Isis who used eggs and sulphur while holding a torch and repeating a prayer. Pliny, in his *Historia naturalis* (**6**. 50), also stated that sulphur had its place in religious ceremonies, and that it was used in fumigating houses. Pliny said:

> Sulphur is employed ceremoniously in the hallowing of houses, for many are of the opinion that the odour and burning thereof will keep out all enchantments—yea, and drive away any foul fiends and evil spirits that do haunt the place.

Pliny regarded sulphur as one of the most singular kinds of earth, and an agent of great power on other substances. He said that sulphur was obtained from the volcanic islands between Sicily and Italy; and from the Isle of Melos; and that it was mined from the hills in the territories of Neapolis and Campania. When mined, the sulphur was purified by fire. Pliny said that there are four kinds of sulphur: *viz.* (i) *Sulfur vivum*, or *apyron*—introduced by fire—occurs in solid masses or blocks and is used for medical purposes; (ii) *gleba*, or glebaceous sulphur, is used in the workshops of fullers; (iii) *egula* is used for fumigating wool; and (iv) sulphur that is used principally in the preparation of matches—*vide* **8**. 51, 38.

Pliny indicated fourteen medicinal virtues of sulphur, which, he said, are also to be perceived in certain hot mineral waters. Pliny added that lightning and thunder are attended with a strong smell of sulphur, and the light produced by them has a strong sulphureous complexion. No substance, said he, ignites more readily than sulphur, a proof that there is in it a great affinity to fire—*neque alia res facilius accenditur; quo apparet ignium vim magnam etiam ei inesse.* This statement was translated by a writer of the phlogiston period, seventeen centuries later: "Sulphur is the most inflammable substance known; a fact which makes it evident that sulphur contains much phlogiston."

The terms ἄπυρον and πεπυρωμένον are taken to indicate that the Greeks knew how to refine sulphur, although the operation is not mentioned by either Dioscorides or Pliny. It has also been argued, less probably, that these terms were intended to distinguish between flowers of sulphur and the wax-like variety. G. Agricola described the extraction of sulphur from the native earth. Two pots placed one above the other were arranged so that the upper pot had a perforated bottom, and it was alone heated by the fuel. The sulphureous earth, or pyrites, was placed in the upper pot, *A*, with a luted lid, *C*, Fig. 1. As the sulphur melted, it dripped into the lower pot, *B*, which might also contain water. Sometimes the lower or receiving pot was buried in the ground as illustrated by Fig. 1, given by G. Agricola.[1] He added to Pliny's list of the uses of this substance:

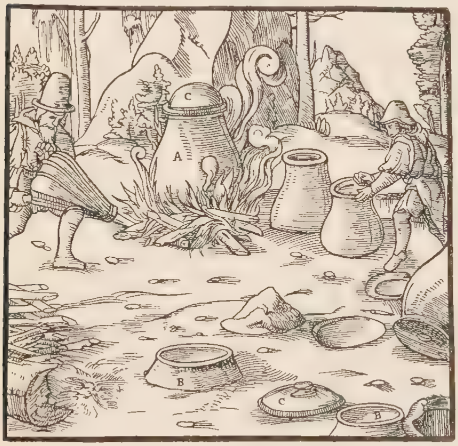

FIG. 1.—The Extraction of Sulphur in the Sixteenth Century.

> Sulphur also enters into the composition of gunpowder—an *execrable invention* which has introduced a new kind of warfare for it enables missiles of iron, steel, or stone to be shot far away.

The twelfth-century Latin version of the Arabian Geber—*Summa perfectionis magisterii*—thus refers to sulphur:

> Sulphur is a fatty earth thickened in the mine by boiling until it has hardened and become dry; and when it has hardened it is called sulphur. It has a very strong composition and is of uniform substance in all its parts because it is homogeneous; and therefore its oil is not removed by distilling as is the case with other substances possessing oil. . . . Sulphur can be calcined only with great loss. It is as volatile as a spirit. When calcined with sulphur, all metals increase in weight, in a manner which cannot be questioned, for all the metals can be combined with sulphur, excepting gold, which combines only with difficulty. Mercury combines with sulphur producing a sublimate of *uzufur* or cinnabar. Sulphur usually blackens the metals, but it does not transmute mercury or silver as some philosophers imagine.

In his twelfth-century *Compositum de compositis*, Albertus Magnus also described the preparation of cinnabar in this manner; and he made a special study of the action of sulphur on the metals. In his *De rebus metallicis et mineralibus*, he was led to apply the word affinity—*propter affinitatem naturæ metalla aduit*—to connote that relationship between combining substances which is the cause of their union. Geber, in his *De inventione veritatis*, also mentioned the preparation of *milk of sulphur*—*lac sulfuris*:

> Rub very finely some natural sulphur, clear and gummy, and boil in lye made from powdered ashes and natural chalk until it appears transparent. This done, stir with a

stick and carefully remove that which has come out with the lye by leaving the thickened part beneath. Cool the extract a little, and put on it a fourth part of good vinegar, and lo, the whole will congeal like milk. Remove the clear lye as far as you can, and dry off the residue by a slow fire.

Later chemists spoke about milk of sulphur as a well-known substance; and Basil Valentine[2] also referred to *flowers of sulphur—flores sulfuris*—as a well-known product. The preparation of the sublimate—flowers of sulphur—was described by G. Agricola, and A. Libavius.

The peculiar properties of sulphur—namely, its combustibility, its association with metals, and its power of uniting with metals to form a number of coloured compounds—led to the view that this element has a mysterious relationship with the metals; and it was soon considered to be a necessary constituent of all metals. Hence, the sulphur of the *materia prima* theory of matter came to represent the principle of combustion, in the same sense that *sel* represented the principle of fixidity and solidity, and *mercury* the principle of gaseity and liquidity—*vide* **1**. 1, 12. Hence, the *sulphur* of the philosophers, advocated by, say, J. R. Glauber in the middle of the seventeenth century, was a mystic, inscrutable spirit, not the sulphur of the working alchemist. In 1675, N. Lemery, in his *Cours de chimie*, opened a chapter on this substance: "Sulphur is a kind of bitumen that is found in many places in Italy and Spain." J. G. Wallerius said that sulphur *nil aliud est quam inflammable concentratum forma solida seu terrestre*. This is virtually the hypothesis expounded by Geber, and J. Kunckel said:

Sulphur consists firstly of a fatty earth which is a sort of combustible oil of a kind which is found in all vegetables; and secondly of a fixed volatile salt and a certain thick earthiness.

In the sixteenth and seventeenth centuries, chemists—Paracelsus, N. de Lefèbure, C. Glaser, etc.—regarded sulphur as a resinous or fatty earth which contained sulphuric acid; J. Kunckel also believed that sulphuric acid and a combustible substance are the chief constituents of sulphur; and this hypothesis was advocated by J. R. Glauber in the middle of the seventeenth century. G. E. Stahl taught that sulphur itself is a compound of sulphuric acid and phlogiston: Sulphur $\rightleftharpoons$Phlogiston+Sulphuric acid. This reaction played an important part in establishing the phlogiston theory—**1**. 1, 15. L. A. Emmerling adopted R. Kirwan's view that sulphur contains 40 per cent. of phlogiston and 60 per cent. of vitriolic acid, and remarked that the antiphlogistians considered sulphur to be *ein chemisch einfacher Körper*. After A. L. Lavoisier and other antiphlogistians had demonstrated the fallacy in G. E. Stahl's hypothesis, sulphur was regarded as an elemental form of matter. Thus, in 1801, R. J. Haüy stated that, according to the results of *la chimie moderne, soufre est un corps simple*. Some rival hypotheses were suggested—*e.g.* F. R. Curaudau[3] supposed sulphur to be a compound of carbon, nitrogen, and hydrogen; C. Girtanner guessed oxygen and hydrogen; and H. Davy, that sulphur is a compound of small quantities of oxygen and hydrogen with a basis that yields the acids of sulphur on combustion. Hydrogen is produced in such quantities from sulphur by voltaic electricity that it cannot well be considered as an accidental ingredient, and he likened sulphur to a hydrocarbonaceous vegetable matter. This was supported by W. Clayfield's and A. B. Berthollet's observations. H. Davy gave up the hypothesis that sulphur contained oxygen after his study of the action of chlorine on that element; J. Dalton argued against the idea; and J. L. Gay Lussac and L. J. Thénard proved that sulphur must be regarded as an element.

T. Cross[4] thought that by electrolyzing a mixture of silver sulphate and sulphide he had transmuted sulphur into a new element which he called *bythium*, but H. Alexander contradicted the results which T. Cross had reported.

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[4] T. Cross, *Wied. Ann.*, **46**. 171, 1893; *Elektrochem. Zeit.*, **3**. 1, 112, 1897; **5**. 48, 1898; H. Alexander, *Zeit. Electrochem.*, **5**. 93, 1899.

§ 2. The Occurrence of Sulphur

Sulphur occurs in nature free and combined. According to the estimates of F. W. Clarke,[1] and F. W. Clarke and H. S. Washington, the igneous rocks of the earth's 10-mile crust contain 0·052 per cent. of sulphur, and 46·42 per cent. of oxygen; and the sedimentary limestones, 0·09 per cent. of sulphur, and 42·57 per cent. of CaO. The average amount of SO_3 in shales is 0·64 per cent.; in sandstones, 0·07 per cent.; and in limestones, 0·05 per cent. The estimated average for the earth's lithosphere is 0·049 per cent. of sulphur, and 0·026 per cent. of SO_3 when that of silica is 59·08 per cent. Otherwise expressed, the earth's lithosphere —or 10-mile crust—has 0·06 per cent. of sulphur (oxygen, 46·46 per cent.); the hydrosphere, 0·09 per cent. (oxygen, 85·20 per cent.); and the general average for lithosphere, hydrosphere, and atmosphere is 0·06 per cent. (oxygen, 49·20 per cent.); J. H. L. Vogt estimated that the igneous rocks of the earth's crust contained 0·6 per cent. of sulphur (oxygen, 47·2 per cent.). H. S. Washington gave 0·64 per cent., and W. Vernadsky gave 0·54 for the percentage amount, and 0·1 for the atomic proportion.

Sulphur also occurs in extra-terrestrial regions. As indicated by E. F. F. Chladni,[2] and E. Cohen, several people have mentioned the blue flame and sulphureous smell of meteorites which have just fallen; E. Mathias said that the colours most frequently observed with thunderbolts are those of black bodies cooling, *i.e.* yellow, orange, or red. In many cases, however, blue, or a colour produced by superposition of blue on one of the preceding, is observed; these are attributed to burning sulphur, possibly arising from sulphur-containing organic matter in the atmosphere. The blackening of gilded objects, and the nature of odours observed in some cases, support this conclusion. Free sulphur to the extent of 1·24 per cent. was reported by H. E. Roscoe in the Alais meteorite, and lesser amounts in other meteorites have been indicated by F. Wöhler, J. N. Lockyer, F. Pisani, N. Teclu, J. L. Smith, C. U. Shepard, and C. Reichenbach. Scores of meteorites have been observed to contain metal sulphides, principally pyrites—*vide* iron. D. Brewster,[3] and C. A. Young thought that they recognized the occurrence of the spectral lines of sulphur in the solar spectrum, but H. A. Rowland, and M. N. Saha concluded that the spectral lines of the sun show no indication of sulphur. J. N. Lockyer discussed the indications of sulphur in the spectral lines of some of the hotter stars; and I. S. Bowen, in nebulæ.

The occurrence of combined sulphur in the form of hydrogen sulphide and sulphuric acid is indicated below, and its occurrence as sulphates, and sulphides is discussed in connection with the individual metals. The great repositories of sulphur are the beds of gypsum, limestone, and associated rocks, or else in the regions of active and extinct volcanoes; thus, it is found in the encrustations of fumaroles and other volcanic vents; and in sulphurous springs where it falls to the bottom as a light-coloured mud; in many old crater lakes where the bottom is covered with muds and clays mixed with sulphur. There are thus two main types of native sulphur: (1) *The solfataric type* found in lava fissures and in extinct volcanic vents (Japan, Mexico). Deposits of this type are forming at the present day in volcanic districts from the mutual action of hydrogen sulphide and sulphur dioxide which occur among volcanic gases. According to C. W. Vincent,[4] the water from a spring at Krisuvik, Iceland, is ejected, with a hissing noise, to a height of 5–8 ft., and is accompanied by steam impregnated with hydrogen sulphide and sulphur dioxide. The water subsequently deposits sulphur, and in many places the surface of the ground has a crust of sulphur 2–3 ft. thick. This was at one time collected and exported. G. Mackenzie, speaking of the "living" sulphur mines in this region, said:

> It is impossible to convey adequate ideas of the wonders of its terrors. The sensations of a person, even of firm nerves, standing on a support which feebly sustains him, where literally fire and brimstone are in incessant action, having before his eyes tremendous proofs of what is going on beneath him, enveloped in thick vapours, his ears stunned with thundering noises, can hardly be expressed in words, and can only be conceived by those who have experienced them.

(2) *The gypsum type.*—The sulphur appears to have been liberated from gypsum by the reducing action of bituminous matters found associated with the gypsum.

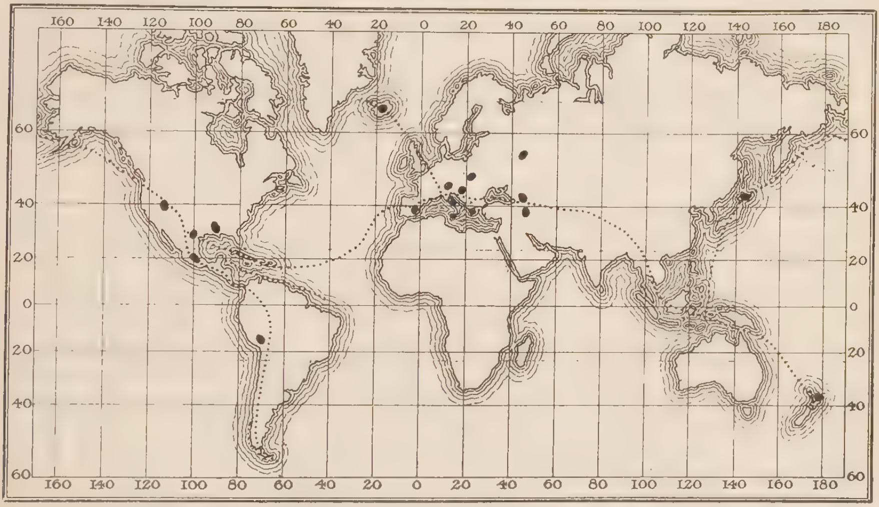

FIG. 2.—The Geographical Distribution of the Sulphur Deposits. (The dotted lines are Imaginary Lines through the Chief Regions of Volcanic Activity.)

Calcium sulphide is probably formed from the sulphate; and this, by the action of water and carbon dioxide, forms sulphur, calcium carbonate, and hydrogen sulphide. The Sicilian deposits, and perhaps the more important sulphur deposits, are of this type. F. Rinne [5] reported a sulphur from Java containing 29·22 per cent. of arsenic which he called *sulphurite*.

Occurrences have been reported in various parts of the world. Most of the districts where sulphur is profitable are not far from the dotted lines, Fig. 2, representing regions of past or present volcanic activity. These countries are the world's sulphur producers. The world's production of sulphur in long-tons is shown in Table I.

TABLE I.—THE WORLD'S PRODUCTION OF SULPHUR.

	1909	1914	1919	1923	1925
Austria . .	12,856	20,314	10,173	15,136	—
Chile . . .	4,508	10,008	18,910	11,380	8,929
France . .	2,900	—	2,222	272	147
New Zealand .	—	—	—	—	269
Greece . .	1,000	Nil	2,238	2,243	1,180
Italy . . .	435,060	377,843	226,126	256,342	286,249
Japan. . .	36,317	75,308	67,382	37,408	89,582
Spain . . .	21,750	47,180	89,586	66,371	77,711
United States .	303,000	347,491	680,800	1,644,904	1,409,262
Total . . .	817,391	878,144	1,097,437	2,034,056	1,873,329

Europe.—There are no deposits of sulphur of commercial importance in **Great Britain,**[6] a little has been found associated with the gypsum of Newark, Nottingham, and in Cornwall, Derbyshire, Westmoreland, and Cumberland; and concretions have been reported in the Carboniferous Limestone of **Ireland.** In **France,**[7] marls containing sulphur are mined in the departments of Bouches-du-Rhône and Vauclase for the use of vineyards; there are small occurrences in several other departments; and there is a small deposit of sulphur associated with the gypsum of Biabaux near Marseilles. There are deposits of sulphur in **Spain** [8] in the provinces of Mercia, Almeria, and Albacete. The sulphur is here associated with gypsum and marl. **Italy** [9] is the most important sulphur-producing country in Europe, and it now ranks second to the United States in the world's production. Most of the sulphur is obtained in Sicily from a belt extending over 100 miles from Mount Etna on the east, to Girgenti on the west. The centre of the industry is at Caltanisetta. The sulphur occurs in veins, pockets, and impregnations associated with gypsum and bituminous marls. G. Baldassarri found it in the Zoccolino Grotto of Tuscany; J. Pitton de Tournefort, in a grotto at Milo; and G. de Dolomieu, in a cave on Ætna. It also occurs in the volcanic islands near Sicily; in the Solfatara near Naples; in the bituminous deposits near Bologna; etc. A few occurrences have been reported in **Germany,**[10] **Belgium,**[11] **Iceland,**[12] **Galicia,**[13] **Macedonia,**[14] and **Greece.**[15] **Cyprus** produced 12 tons in 1920. Deposits occur in **Russia,**[16] **Austria,**[17] **Hungary,** and **Switzerland.**[18] There is none in **Norway.**

Africa.—A deposit of sulphur occurs at Guelma,[19] **Algiers;** a number of deposits have been reported from **South** and **West Africa**; [20] Bahar el Saphingue, **Egypt; Teneriffe;** and the Islands of **Tor** and **Bourbon.**

Asia.—Occurrences of sulphur have been found in the **Transcaspian** district; [21] in **Palestine,**[22] **Asia Minor,**[23] **Persia,**[24] **Mesopotamia,**[25] and **Central Asia.**[26] Deposits of sulphur have been reported at many places in **India,**[27] notably at Ghizri Bunder in the province of Golkurt near Karghari on the Mekran Coast. The most important mine is near Sanni, in the Kachhi district of the Kelat State, Baluchistan. Sulphur also occurs in **Burma,**[28] at Mawsün in the Southern Shan States, **Java,**[29] **Celebes,**[30] the **Philippine Islands,**[31] and **China.** **Japan** [32] is an important producer of sulphur. The deposits are of volcanic origin, and occur as sulphur-bearing clays in the beds of lakes of ancient craters, or in muds which have been ejected during periods of volcanic activity. A little sulphur also occurs in the vicinity of volcanic vents and fumaroles. The most important mining area is in Hokkaido; there are sulphur mines along the Kirishima volcanic zone; and there are many deposits in the north of Honshu. There are no sulphur deposits on Shikoku, and none is mined in Korea. A little sulphur is mined in several of the Kurile Islands; and in the vicinity of Daiton volcano, Formosa.

Australasia.—G. H. F. Ulrich [33] noted the occurrence of sulphur in **Victoria;** R. W. E. MacIvor, in **New South Wales;** A. McIntosh Reid, in **Tasmania;** and there is a deposit at White Island, **New Zealand.** Deposits have been also reported on some of the **Pacific Islands,**[34] Vanua Levu, New Hebrides, Sandwich Islands, etc.

South America.—There is a number of important sulphur deposits of volcanic origin in **Chile,**[35] where the majority are situated at high altitudes. The deposit worked on Mounts Olca and Chupiquina are at altitudes of 17,000 to 18,000 ft. above sea-level. There are also deposits at Mounts Ollagüe and Tacora. Small occurrences have been noted in the **Argentine, Peru, Ecuador, Colombia, Brazil, Trinidad,** and **Martinique.**[36]

North America.—Occurrences of sulphur have been reported in **Mexico.**[37] The largest producer of sulphur is the **United States** [38] and there are deposits in California, Nevada, Utah, Wyoming, Texas, Louisiana, Georgia, Virginia, Maryland, Pennsylvania, and Michigan; but 98 per cent. of the total output occurs in the deep-lying sulphur beds of Louisiana and Texas. There are also occurrences in Unalaska, the Akun Islands, and in the Katmai region, Alaska—*e.g.* as incrustations about the fumaroles of the valley of Ten Thousand Smokes. There are deposits in **Canada** [39] in the provinces of Nova Scotia, Ontario, Alberta, British Columbia, and in the district of Mackenzie.

C. Vischniac [40] found some sulphur in iodine. W. Prandtl discussed the difficulties attending the preparation of hydrogen free from sulphur. The occurrence of sulphur in the tissues of animals and man has been discussed by E. and H. Salkowsky, etc. H. Schulz found that in the dried organs of a man aged 39 the percentage of sulphur varied from 0·57 in the brain to 1·03 in the jejunum. In the muscles of different animals, the percentage varied from 0·86 to 1·33; in the human aorta, from 0·47 to 0·67; and in the human vena cava, from 0·28 to 0·73. The sulphur in the liver cells of oxen was estimated by F. Krüger and co-workers; they also found the liver cells of man to contain 2·41 per cent. of sulphur; and of newly born children, 3·56 per cent. In a case of fatty degeneration of the liver, there was present 2·18 per cent. of sulphur. The sulphur in egg albumen was discussed by E. Drechsel,[41] P. N. Raikow, E. Baumann, E. L. Salkowsky, and A. Krüger; in pig's fat, by G. Mariani; in cow's milk, by G. Sartori; in urine, by R. Lépine and co-workers, A. Heffter, E. Petry, S. Bondzynsky and K. Panek, and F. H. Thiele; in the fæces, by E. L. Salkowsky, and F. von Oefele; in cystine, by W. F. Hoffman and R. A. Gortner; in human hair, by P. N. Raikow, and F. Düring; by H. Weiske, in bird's feathers; and in wool, by H. Strunk and H. W. Priess, P. N. Raikow, and E. Grandmougin. P. Mohr found the following percentage amounts of sulphur: Woman's hair—dark blonde, 4·95; girl's hair—dark brown, 5·34; boy's hair—red blonde, 4·98; boy's hair—red, 5·32; rabbit's hair, 4·01; calf's hair, 4·35; horsehair, 3·56; pig's hair, 3·59; sheep's wool, 3·68; goose feathers, 2·59–3·16; pig's hoof, 2·69; calf's hoof, 3·57; ox hoof, white, 3·49; ox hoof, black, 3·45. The sulphur of wool is contained in the keratin. Dry wool readily absorbs hydrogen sulphide, and as such is easily oxidized to sulphurous acid. Hence the reports that sulphites are present in wool, and that the keratin mol. contains sulphite. E. Laborde found approximately 0·2 per cent. of sulphur in the skin of three children; and in the healthy skin of another who had died from poisoning by sulphuric acid, there was 0·15 per cent., whilst the burned areas of the skin contained 0·37 per cent. The occurrence of sulphur in plants—onions, garlic, mustard, horse-radish, oils, etc.—was discussed by M. Berthelot and G. André,[42] G. Cugini, T. Jamieson, J. M. H. Munro, and G. Tammann. A. R. Thompson found sulphur in the rice-plant.

J. H. and C. J. Cravenhorst [43] observed that sulphur is produced when a decoction of vegetable matter is allowed to stand in contact with sodium sulphate—*vide infra*, hydrogen sulphide. The occurrence of granules of sulphur in the cells of some kinds of *Beggiatoa* was noted by C. Müller. S. Winogradsky's diagram of the *Beggiatoa alba*, Fig. 3, shows the sulphur granules present in the cells. In 1870, G. Hinze observed granules of sulphur in the cells of the algæ *Ulothrix*, and *Oscillaria*. A. Corsini showed that the sulphur is in the colloidal form. F. Cohn found that the sulphur is always present in certain types of bacteria found in sulphur springs, where they abound in the white, slimy masses there present. Sulphur is indeed a product of the life action of certain bacteria—*e.g.* the *Beggiatoa alba*, *Chroma-*

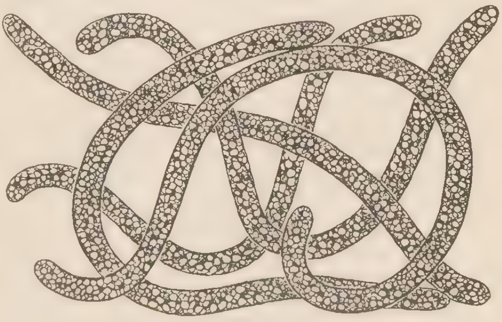

FIG. 3.—Beggiatoa alba (×1000).

tium okeini, etc. Just as plants and animals derive energy and heat by the oxidation of carbon, so do these bacteria appear to obtain their energy and heat by the oxidation of sulphur. It is estimated that roughly 25 per cent. of their body is sulphur. S. Winogradsky said that the *Beggiatoa* do not make sulphur by reducing sulphates to hydrogen sulphide, and partially oxidizing the hydrogen sulphide to water and sulphur; rather do they oxidize the hydrogen sulphide to sulphur and water. They can be cultivated in a very dil. soln. of hydrogen sulphide; conc. soln. are harmful. The sulphur stored in the cells can be oxidized to sulphates. The members of another kind of sulphur bacteria can oxidize thiosulphates to sulphuric acid: $3Na_2S_2O_3+5O=2Na_2SO_4+Na_2S_4O_6$. According to D. C. Harrison, hydrocyanic acid inhibits not only the aërobic but also the anaërobic oxidation of sulphur-compounds. The addition of traces of copper and iron to purified sulphur-compound groups accelerates their aërobic and anaërobic oxidation. The activation of oxygen is not a necessary process, nor does it seem that the catalytic action of the metals is due to the activation of oxygen. D. C. Harrison assumes that the catalysis of the oxidation of the sulphur compound group by metals is effected by the alternate oxidation and reduction of the catalytic metal by means of which hydrogen is made available for acceptance by molecular oxygen or by methylene blue. The reduction of methylene blue by sulphur compounds may take place to an appreciable extent even in the complete absence of catalytic metals.

Very little is known about the bacteria which oxidize the sulphides in soils. N. D. Zelinsky associated the thick layers of iron sulphide on the bottom of the Black Sea with the action of various micro-organisms on the ooze, and one of them, the *Bacterium hydrosulfureum ponticum*, can produce hydrogen sulphide from sulphates, sulphites, etc. L. Elion, however, emphasized the fact that this bacterium is not able to attack sulphates. Actually, the number of bacteria able to reduce sulphates is small. M. W. Beyerinck showed that the alleged reduction of sulphates by bacteria is actually an oxidation of organic matter with the aid of the oxygen from the combined sulphate: $2C+RSO_4+O=RCO_3+CO_2+S$, and the energy is derived from the combustion of the organic matter. This particular bacterium was called the *Spirillum desulfuricans* –afterwards *Microspira desulfuricans*. A. van Delden found the same bacterium in some vegetable mould, and the deposit of iron sulphide in the Wadden shallows of the Dutch coast was formed by the hydrogen sulphide produced from the bacterium which he named *Microspira æstuarii*. B. L. Issatchenko found this bacterium in the Black Sea ooze. A. Rank found the *Microspira desulfuricans* in sea sand; and C. A. H. von Wolzogen Kühr, in the sand and clay of the Dutch dunes. L. Elion found yet a third sulphate-reducing bacterium which he called *Vibrio thermodesulfuricans* with an optimum temp. of 55°—*vide infra*, the occurrence of hydrogen sulphide.

The occurrence of sulphur in coals, and in the products of the dry distillation of coal, has been discussed by W. Wallace,[44] etc.; in oil-shales, by E. P. Harding; in petroleum and gasoline, by C. F. Mabery and A. W. Smith,[45] F. Challenger, etc.; in iron,[46] and in natural waters by H. Moissan.[47] H. Moissan found that the water of the Bordeu Spring, Luchon, contains no hydrogen sulphide, and this gas, present in the air at the well, is considered to be a secondary product of the action of the carbon dioxide of the air on the sodium sulphide present in the water. The water has free sulphur in soln., and the vapour evolved from this water contains traces of hydrogen sulphide and of sulphur dioxide as well as some free sulphur. The free sulphur may be derived from three sources: (1) vaporization of sulphur from the water, (2) slow combustion of the hydrogen sulphide, and (3) the interaction of the hydrogen sulphide and the sulphur dioxide.[48]

Sulphur as a volcanic sublimate is produced by a reaction between sulphur dioxide and hydrogen sulphide. It is also formed by the incomplete combustion of hydrogen sulphide: $2H_2S+O_2=2H_2O+2S$, as shown by G. F. Becker,[49] E. Onorata, and J. Habermann; and by the action of steam on sulphides: $3PbS+2H_2O$

$=3Pb+2H_2S+SO_2=3Pb+3S+2H_2O$, and by the action of steam on hydrogen sulphide observed by A. Gautier. J. Papish found that sulphur dioxide is reduced to sulphur by methane at elevated temp.; consequently, the sulphur occurring in volcanic regions may, in part, be formed by the reduction of sulphur dioxide by methane, carbon monoxide, or hydrogen—all of which occur in volcanic exhalations. The sulphur deposits common about mineral springs are also due to the imperfect oxidation of hydrogen sulphide, which is produced by the action of acidic waters on sulphides, or by the reduction of sulphates by micro-organisms, etc., as advocated by E. Plauchud, A. Étard and L. Olivier, and W. F. Hunt. A. Daubrée, F. Hoppe-Seyler, L. Baldacci, G. Bischof, and R. Travaglia considered that the Sicilian sulphur has been produced by the action of organic matter—the remains of marine animals—on the sulphates. A. Krümmer and R. Ewald found a large cavity in gypsum met with in the Barsinghausen mines was lined with bitumen, resting on which were large crystals of sulphur. Between the gypsum and the bitumen was a zone of calcium carbonate; and the gases in the cavity contained hydrogen sulphide and hydrocarbons. The sulphur had no doubt been formed by the reducing action of the hydrocarbons on the gypsum, for example: $CaSO_4+CH_4=CaS+CO_2+2H_2O=CaCO_3+H_2S+H_2O$; followed by $2H_2S+2H_2O+O_2=4H_2O+2S$. The deposits of sulphur in Sicily, which are associated with gypsum and outbursts of gas containing hydrocarbons and carbon dioxide, have probably been formed in a similar manner. Attempts have been made to explain the occurrence of sulphur and gypsum without assuming that one is derived from the other. A. von Lasaulx, and G. Spezia assumed that the sulphur was deposited from water containing hydrogen sulphide and calcium carbonate during the concentration of fresh water basins. G. Spezia, and A. Béchamp showed that when hydrogen sulphide acts on water and calcium carbonate under press., calcium hydrosulphide is formed, and when the soln. is evaporated calcite, gypsum, and sulphur are formed. R. Brauns, and L. Dieulafait also argued that when sulphuretted waters act on sedimentary limestones, sulphur and gypsum are produced. H. Sjögren, and O. Silvestri found in a liquid inclusion of gypsum, a fluid like sea-water, and hydrogen sulphide. The deposits of sulphur in Western Texas are associated with gypsum, and with water containing hydrogen sulphide. E. M. Skeats showed that in some cases, the waters from sulphur-beds are strongly acidic owing to the presence of sulphuric acid. E. Dittler said that native sulphur may be produced in some cases by the action of steam on pyrites or marcasite. The general subject has been discussed by G. Spezia, B. Doss, F. W. Clarke, W. F. Hunt, E. Cortese, O. Stutzer, W. Lindgren, and G. B. Richardson.

The sulphur cycle.—W. Lindgren[50] has well emphasized the fact that in nature a large part of the sulphur is continually in movement, changing from sulphide to sulphate with local reversions to native sulphur, and from sulphate back to sulphide. He follows the cycle somewhat as follows: All active volcanoes give off enormous quantities of hydrogen sulphide some of which is oxidized to form sulphur dioxide and then the trioxide. The resulting sulphuric acid descends to the earth with rain to form sulphates by reacting with the basic rocks. A part of the hydrogen sulphide is reduced to native sulphur. All intrusions contain sulphur compounds part of which are fixed as metal sulphides—*e.g.* pyrites—which fill veins or impregnate adjacent rocks; or else as sulphates—*e.g.* barytes, and anhydrite. Some of the silicated waters which come to the surface carry hydrogen sulphide in soln., and this gives rise to accumulations of native sulphur about the vent of springs.

When the basic sulphide rocks are exposed at the surface, they are oxidized to soluble sulphates—*e.g.* iron, aluminium, magnesium, zinc, calcium, potassium, and sodium—which find their way to the sea. The less soluble sulphates—*e.g.* lead sulphate or the basic iron sulphates—linger behind. In the average river waters, sulphates are present in relatively large amounts, and enormous quantities are discharged into the ocean, so that the sulphates would predominate over the chlorides in the waters of the sea were it not for the continuous reduction of sulphates to sulphides along the littoral—particularly muddy shores rich in organic matter. Sulphur as iron sulphide is plentiful in shore deposits, and in some deep closed basins, like the Black Sea, similar reducing conditions obtain at the bottom, and the mud at the bottom is rich in iron sulphide.

The evaporation of sea-water or lake-water in closed basins results in the deposition of calcium sulphate which forms nearly all the known beds of gypsum. When meteoric waters loaded with hydrocarbons act on calcium sulphate, the sulphate is reduced to sulphur. The sulphate may be similarly reduced by bacterial activity.

The muds and silts, rich in iron sulphide, largely as marcasite, are compressed, raised, and folded by geological processes to form shales and sandstones. The sulphide is then attacked by oxidizing soln., converted into soluble sulphates and again carried back to the sea. The meteoric waters circulating at deeper levels, extract sulphates from uplifted sediments—limestone, slate, or silt—near the surface, and, lower down, the sulphides of hydrogen, iron, zinc, lead, copper, cadmium, cobalt, or nickel. The sulphides may be deposited elsewhere as in the zinc and lead sulphide deposits on the limestone of the Mississippi Valley.

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§ 3. The Extraction of Sulphur

The *sulphur earth* occurs in Sicily in lodes mixed with limestone and gypsum. The amount of sulphur in "workable" ore varies from 8 up to about 25 per cent. The sulphur is separated by heating the ore and allowing the molten sulphur to flow away from the mineral impurities. This is effected by stacking the ore on the sloping floor of a circular kiln without a permanent roof. The kilns are called *calcaroni*. In stacking the ore, air spaces are left at intervals to secure ventilation. The stack is covered with powdered or burnt ore. The sulphur is ignited near the bottom. A portion of the sulphur acts as fuel, and melts the remainder which collects at the lowest point of the inclined bottom of the kiln. After about five days, a plug at the lower end of the kiln is removed, and the sulphur is run into small wooden moulds. The opening is closed, to be reopened day by day until, in from three to five more days, the sulphur ceases to flow. About one-third of the sulphur is lost in the calcarone system of extraction. It is, however, cheaper to use the sulphur as a fuel than to import coal. The loss, however, is excessive even then, and in consequence, the calcarone method has been displaced by more economical kilns. The kiln devised by R. Gill[1] is mainly employed. This consists of an oven covered by a cupola called a *cell*. Inside is a small cupola within which a coke fire burns. Each cell holds up to about 5 cubic metres of ore. About six cells make a *battery*. The gases generated in the first cell pass by lateral channels into the next cell. When the liquation is completed in the first cell, the contents of the second cell have been heated to the ignition point of the gases. This cell is treated as in the case of the first one and so on in rotation. It is claimed that at least an 80 per cent. yield is attained by these kilns; the time required for each cell is 3–4 days; and gases heavily charged with sulphur are not lost in the atmosphere, and in consequence the work can be continued all the year round without danger to the crops of the farmers. The process was studied by A. Ricevuto and M. Buogo. G. A. Strover described the simple distillation process employed in Upper Burmah. The processes for extracting sulphur in Sicily have been described by E. Jungfleisch, B. Bruhn, S. Aichino, W. C. Phalen, etc.

The difficulties attending the mining of sulphur at Louisiana, led H. Frasch[2] to devise a totally new method of extraction, which has removed from Sicily the domination of the conditions regulating the world's supply of sulphur. By means of rigs and drills, holes are bored to the sulphur deposit in a way similar to those employed in boring for oil. Sulphur melts at 116°. The subterranean sulphur is melted by superheated steam, which is conveyed through a 6-in. pipe to the sulphur bed, Fig. 4. The molten sulphur collects as a pool at the bottom of this pipe. Enclosed in this pipe is another 3-in. pipe through which the molten sulphur—or rather an emulsion of sulphur and air—is raised to the surface by compressed air (250 lbs. per sq. in.) forced through an inner 1-in. pipe. The molten sulphur is then conveyed to a wooden bin, where it solidifies. The sulphur is of a high degree of purity—99·93–99·98 per cent. sulphur—and it contains only a trace of water. The process is applicable only to deposits rich in sulphur—say 60 per cent.—and therefore is not available for the Sicilian earths.

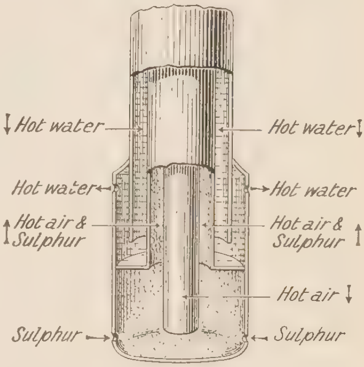

FIG. 4.—H. Frasch's Sulphur Pump.

The geyser-like craters in the Bungo province, Japan, emit sulphurous fumes intermittently. During inactive periods, the Japanese have placed pipes in the ground, and in crevices about its craters, so as to collect the fumes during the active periods. The fumes are led into suitable reservoirs, and the liquefied sulphur flows from there in conduits, and solidifies down the side of the mountain. The sulphur is then broken into fragments and sold as *Bungo sulphur*.

A number of other proposals has been made for extracting sulphur from earths. J. G. Whitlock[3] suggested distilling the sulphur from large vessels. C. Bellman proposed extracting the sulphur with carbon disulphide. A. Walter, and F. Dickert patented systems of liquating sulphur from the sulphur-earth. W. Gritti melted the sulphur from the earth by heating with superheated steam. The idea was modified by F. W. Becraft and A. L. Genter, W. D. Huff, the Texas Gulf Sulphur Co., E. F. White, R. P. Perry, and W. E. Clifford and T. H. Green; A. K. Sedgwick melted the sulphur in the earth by superheated steam, and separated the molten sulphur by centrifugal action. M. de la Tour de Brenil heated the earth with a 66 per cent. soln. of calcium chloride at 120°, and collected the liquated sulphur. A. F. Lucas and G. M. S. Tait obtained the heat for melting the sulphur in the earth *in situ* by partially burning the sulphur in the deposit by a mixture of air and carbon dioxide, and forcing the molten sulphur to the surface by gas press. W. D. Huff melted the sulphur from the earth *in situ* by electrical heaters; and R. Fleming had a modification of the idea. K. M. Baum melted the crude mixture in the presence of an aq. soln. of zinc chloride of such a sp. gr. that the molten sulphur rises to the surface.

E. Dittler [4] said that some colloidal sulphur is produced by the prolonged action of steam on pyrites and marcasite, and that in some cases native sulphur may have been produced by a similar action. Sulphur obtained by the distillation of pyrites or other metal sulphide is commercially possible only in a few cases. A. Walter partially roasted the ore in a suitable furnace; W. A. Hall heated the ore with steam and a reducing flame; the New Jersey Zinc Co. heated the ore to 600°–800° when the pyrites is converted into the pyrrhotite and sulphur; G. T. Gerlach, O. C. D. Ross, and C. F. Claus heated the ore with superheated steam; L. P. Wright heated the pyrites in an electrically heated retort and found sulphur distilled off, and iron contaminated with sulphur remained; the Rhenania Verein Chemische Fabrik produced sulphur by the action of sulphur dioxide on iron sulphide or pyrites or mixtures which yield iron sulphide on heating above 600°. C. E. Kingsley heated the sulphide with dil. nitric acid (1 : 20); and J. Swinburne electrolyzed the molten sulphide.

Large quantities of free sulphur are produced in the manufacture of coal-gas, or coke-oven gas, where this element accumulates in the iron oxide of the purifying plant. Most of the sulphated oxide is used in making sulphur dioxide, but some may be treated for free sulphur. E. Vaton and A. Zuaznavar [5] distilled the spent oxide in retorts; and A. Derome heated the material to redness while injecting steam into the retort to decompose the cyanides, etc.—sulphur, ammonia, etc., pass to the condensing chambers. P. E. Williams treated the pentoxide with aq. ammonia, the resulting polysulphide was decomposed by heat, and the escaping ammonia was collected and used over again. A number of solvents has been recommended—*e.g.*, boiling acetylene tetrachloride mixed with xylene. The Société d'éclairage used light tar oils; J. J. M. Bécigneul, hot toluene or toluene mixed with carbon tetrachloride; E. J. Hunt and W. F. Gidden, and A. M. Chance and C. Hunt heated the material with sulphuric acid, and extracted the sulphur from the residue by means of a solvent. The dark colour of the product spoils its sale, so that it is nearly always used for making sulphur dioxide. J. J. M. Bécigneul, and the Chemische Fabrik Phönix proposed methods for eliminating the tarry colouring matters. Some sulphur was also produced in the residue from the soda-ash process.

It was proposed by J. H. Vivian [6] to obtain sulphur from sulphur dioxide by passing the gas through red-hot coke; F. Reich experimented on the process in 1858; and several proposed modifications—by E. Will, M. Ruthenburg, L. P. Basset, W. F. Lamouraux and C. W. Renwick, C. S. Vadner, and The American Smelting and Refining Co.—have been based on this reaction. F. R. Carpenter passed a mixture of sulphur dioxide and steam through red-hot coke and produced hydrogen sulphide: $2SO_2+2H_2O+3C=2H_2S+3CO_2$; and $SO_2+H_2O+3C=H_2S+3CO$. The mixture containing hydrogen sulphide was then burnt with the necessary amount of air to produce sulphur: $H_2S+O=H_2O+S$—*vide infra.* N. F. Yushkevich and C. A. Karzhavin studied the reactions: $2SO_2+4CO=4CO_2+2S$, and $2CO=CO_2+C$ at 800° to 1400°. The equilibrium in the former is but slowly attained, particularly at low temp., and for industrial work a catalyst more active than ferrous sulphide is desirable. J. Papish said that sulphur dioxide alone at an elevated temp. is reduced to sulphur. The reduction by carbon monoxide: $SO_2+2CO=2CO_2+S$, was examined by E. Hänisch and M. Schröder, and M. Berthelot. F. L. Teed and co-workers passed the sulphur dioxide mixed with a reducing gas—like producer gas, or water-gas—over a red-hot contact substance like magnesia, calcium sulphate, or ferric oxide: $SO_2+2CO=2CO_2+S$, and $SO_2+2H_2=2H_2O+S$. H. Sanborn and co-workers passed the sulphur dioxide through a tower having a spray of calcium sulphide soln. The mixed calcium sulphide and sulphate, and sulphur are heated when sulphur distils off; and the calcium sulphate when mixed with coke and heated regenerates calcium sulphide. The

Chemische Fabrik Griesheim-Elektron reduced sulphur dioxide or sulphites to sulphur by means of spongy zinc. L. Wöhler and co-workers found that sulphur dioxide reacts with calcium sulphide at temperatures below 1000°, giving the sulphate and sulphur; as the sulphate forms a protective layer on the sulphide, however, the reaction soon ceases. At temp. above 1000°, the products of reaction are lime and sulphur, and the reaction proceeds nearly to completion. The low-temp. reaction can, however, be accelerated by the catalytic action of ferrosoferric oxide. Zinc blende reacts with sulphur dioxide to give sulphur and zinc oxide, which latter forms a protective coating of a kind of basic sulphide on the blende so as to stop the action. Both sulphides of iron react with sulphur dioxide to give ferrosoferric oxide and sulphur. The reaction is rapid and complete, being catalytically accelerated by the ferrosoferric oxide.

The so-called *thiogen-process* of S. W. Young, examined by A. E. Wells, and A. Hutin, is employed for recovering sulphur from the sulphur dioxide of smelter fumes. It depends on the reduction of sulphur dioxide by ethylenic hydrocarbons: $3SO_2+C_2H_4=3S+2CO_2+2H_2O$, which is a slow and incomplete reaction unless stimulated by ferric oxide or calcium sulphide as a catalyst: $2CaS+3SO_2=2CaSO_3+3S$; and $2CaSO_3+C_2H_4=2CaS+2CO_2+2H_2O$. In another process, the fumes are treated with barium sulphide, which produces a mixture of sulphur and a barium oxy-sulphur compound. The mixture is heated to distil off the free sulphur; and then heated with carbon to regenerate the sulphide. N. F. Yushkevich and V. A. Karzhavin, C. G. Collins, A. H. Eustis, G. N. Kirsbom, and E. Will also described processes for recovering the sulphur from smelter-fumes. W. Feld proposed to recover ammonia and sulphur from coal-gas by washing it with a soln. of ammonium tetrathionate—in the so-called *polythionate process*. The tetrathionate is thereby converted into thiosulphate: $(NH_4)_2S_4O_6+2NH_3+H_2O=(NH_4)_2SO_4+(NH_4)_2S_2O_3+S$, and $4NH_3+2H_2O+3SO_2=2(NH_4)_2SO_4+S$. The oxygen necessary for forming sulphate is derived partly from the sulphur dioxide, that is, from the air used in burning the sulphur. When hydrogen sulphide is present in the gas, it provides the necessary sulphur: $(NH_4)_2S_4O_6+3H_2S=(NH_4)_2S_2O_3+5S+3H_2O$. The tetrathionate is recovered by the action of sulphur dioxide and sulphur: $2(NH_4)_2S_2O_3+3SO_2+S=2(NH_4)_2S_4O_6$. The chemistry of the process was discussed by E. Terres and F. Overdick. F. Bayer and Co. obtained sulphur and sulphates from soln. containing sulphites and thiosulphates by adding polythionates and heating the mixture in open vessels; C. Hansen used a similar process. F. Bayer and Co.[7] also obtained it by heating a mixture of water with a sulphite and hydrosulphite in an autoclave at 150° for 4 hrs.: $2NaHSO_3+Na_2SO_3=2Na_2SO_4+H_2O+S$.

Hydrogen sulphide has been frequently examined as a source of sulphur. In C. F. Claus' process, the gas is mixed with the necessary amount of air, and passed over red-hot iron oxide as catalyst, $2H_2S+O_2=2H_2O+2S$. The mixture of sulphur vapour and steam passes out of the kiln into chambers where the sulphur is condensed. E. E. Naef partially oxidized the hydrogen sulphide with activated carbon as catalyst. F. Projahn used bauxite, and titanic iron ore as catalyst; and C. E. Tyers and J. Hedley, a salt or ore of titanium. S. E. Linder oxidized the gas with manganese dioxide. G. H. Hellsing brought the hydrogen sulphide in contact with a conc. soln. of sulphurous acid; W. Feld treated mixed hydrogen sulphide and sulphur dioxide with a compound of a metal—zinc, manganese, or iron—producing an insoluble sulphide, which is decomposed by sulphur dioxide alone or in the presence of air or an oxidizing agent, producing sulphur. He also brought about the reaction between hydrogen sulphide and sulphur dioxide: $2H_2S+SO_2=2H_2O+3S$, in the presence of a heavy coal-tar oil at 40° capable of dissolving the sulphur. Modifications of the process involving the reaction between sulphur dioxide and hydrogen sulphide were described by P. Fritzsche, L. Bémelmans, F. Bayer and Co., S. Norrbin, and R. von Walther. The Badische Anilin- und Sodafabrik obtained sulphur from ammonium sulphide soln. The Deutsche

Petroleum A.G. passed steam or steam mixed with a reducing gas over an alkaline earth sulphide at about 1200°; and the Nürnberg Consortium treated the sulphide with chlorine at a high temp. until the sulphuryl chloride in the distillate suffices for chlorinating the polysulphide formed, which is then decomposed in aq. soln., forming the chloride and free sulphur. The Farbenindustrie A.G. described a continuous process for recovering sulphur from ammonium polysulphide. M. Malzac proposed obtaining sulphur from the sulphides of copper, silver, zinc, cadmium, cobalt, and nickel, and simultaneously forming the hydroxides of these metals, by the action of ammonia and air: $Cu_2S+O+NH_3+nH_2O=2Cu(OH)+S+NH_3+(n-1)H_2O$. The cuprous oxide dissolves in the aq. ammonia. J. Jakobi discussed the cathodic extraction of sulphur from sulphides.

Sulphur can be obtained from sulphates in several ways. R. A. Tilghman[8] patented a process in 1847 for making sulphur dioxide by passing steam over heated gypsum; calcium oxide, sulphur dioxide, oxygen, and a little sulphur trioxide were formed. A similar process was patented by C. Polony in Austria in 1887. H. Precht proposed reducing kieserite by heating it with charcoal: $2MgSO_4+C=2MgO+2SO_2+CO_2$. E. H. Riesenfeld showed that the reaction in part progresses: $MgSO_4+C=MgO+SO_2+CO$. The residue always contained sulphur if less than one at. proportion of carbon was present to one of magnesium. At 750°–850°, the best results were obtained with the 1 : 1 proportion; and at 950°, with the proportion 1·5 : 1. The sulphur was obtained as sulphur dioxide with the exception of a little free sulphur. If a greater proportion of carbon is used, reduction is not complete because the molten sulphide then protects the sulphate from attack. The reduction of gypsum or anhydrite by carbon starts below 500° and is rapid above 700°. The main reaction is: $CaSO_4+3C=CaS+CO_2+2CO$; and similarly with strontium and barium sulphates. This subject was also studied by F. Weeren. The composition of the gas phase is determined by the $CO_2 : CO : C$-equilibrium, but with magnesium sulphate there is a disturbance due to the action of sulphur dioxide on carbon monoxide. The equilibrium: $CaS+H_2O+CO_2\rightleftharpoons CaCO_3+H_2S$ cannot be utilized because at 700° the formation of calcium sulphide is favoured. Gypsum is dehydrated below 800°, but at 800°–1000°, the gypsum is reduced by methane, $CaSO_4+CH_4=CaS+CO_2+2H_2O$; above 1100°, some calcium oxide is produced: $CaS+H_2O=CaO+H_2S$. Excess of steam favours the removal of sulphur at 1200°–1300°. Owing to the dissociation of the hydrogen sulphide, most of the sulphur was obtained as sulphur dioxide or free sulphur, the latter predominating if only a slight excess of water is used. If steam acts on carbon and calcium sulphate at 1200°, the sulphur is converted into sulphur dioxide, and the reaction is six times as fast at 1300°. The reducing action of carbon monoxide and hydrogen on sulphur dioxide produces free sulphur, so that only 50 per cent. of the theoretical amount of sulphur dioxide is obtained even when 850 times the theoretical proportion of steam is used.

J. Zawidsky and co-workers, and W. Dominik studied the thermal decomposition of calcium sulphite with the idea of utilizing the reaction for the production of sulphur dioxide. At 600°, there are the two reactions: $4CaSO_3=CaS+3CaSO_4$; and $CaS+3CaSO_4=4CaO+4SO_2$. There is a condition of equilibrium in which the pressure of the sulphur dioxide depends on the temperature. At higher temp., there is a further reaction between sulphur dioxide and calcium oxide or sulphide, which leads to the separation of sulphur. Above 1150°, the only products of the interaction between sulphur dioxide and calcium oxide are calcium sulphate and sulphur. The decomposition of a mixture of one part of calcium sulphide to three parts of sulphate takes place at temp. which are much lower than those required for the decomposition of pure calcium sulphate. The extraction of sulphur dioxide (*q.v.*) from the sulphates of the alkaline earths was discussed by O. Fuchs, B. Neumann, P. P. Budnikoff, E. V. Tsytovitch, J. H. Frydlender, and H. Molitor. W. Althammer showed that magnesium sulphate is quantitatively reduced when heated with an eq. amount of carbon at 750°, and a 40 per cent. yield of free sulphur is obtained. Even with a fivefold excess of carbon, no magnesium sulphide is obtained, but simply an increase in the yield of free sulphur. The primary reaction is according to the equation, $MgSO_4+C=MgO+SO_2+CO$. The production of sulphur follows the reversible secondary reactions: $2CO+SO_2=S+2CO_2$ and $CO_2+C=2CO$. Illuminating gas, hydrogen, carbon dioxide, benzene vapour, acetylene, and producer gases all reduce magnesium sulphate at 650°–700°. The effect of producer gases depends principally on their hydrogen content. In the case of reduction with hydrogen, over 70 per cent. of the sulphur present is obtained in the free state. The Chemische Fabriken vorm Weiler obtained sulphur dioxide by heating a mixture of calcium sulphate and sulphide: $3CaSO_4+CaS=4CaO+4SO_2$. The reduction of sulphates by coke, or reducing gases was the subject of patents by the Verein Chemischer Fabriken Mannheim, C. Palaschowsky, A. Bamback, J. and F. Weeren, A. M. Chance, C. F. Claus and co-workers, E. Jacobsen, A. Vogt, and the Badische Anilin- und Sodafabrik. It is said that the preparation of sulphur from calcium sulphate was one of the chemical operations rendered necessary by the isolation of Germany during the 1914–1918 war. The sulphur dioxide obtained from the sulphates is converted into sulphur, as previously indicated.

Crude sulphur may be partially purified by melting it in cast-iron vessels, skimming off the coarser particles with a perforated ladle, and after standing some time to allow the fine particles to settle, pouring off the molten sulphur into large wooden moulds to furnish the so-called *rock-sulphur*, or in cylindrical wooden moulds—*roll-sulphur*. Roll-sulphur is usually obtained by distilling the crude sulphur, and ladelling the liquid condensate into suitable wooden moulds. C. A. Schlüter [9] described an arrangement for distilling sulphur placed in a series of retorts arranged in rows in a kind of reverberatory furnace. The head of the retort has a beak passing into a receiver outside the furnace. M. Michel heated the sulphur in a large cast-iron boiler and passed the vapour into a large brick-work chamber, where it condensed as a light, flocculent powder called *flowers of sulphur*, or *flores sulphuris*. Afterwards, as the chamber becomes heated, the sulphur may collect at the bottom in a fused state, and be drawn off by a lateral opening. Usually, however, care is taken to prevent the chamber becoming hot enough to melt the sulphur. The sublimed sulphur collects on the walls and floor, and only a little fused sulphur is found where the neck of the retort enters the chamber. The product is then shaken through sieves of about 40's mesh, and transferred as flowers of sulphur to bags or casks. The coarser particles, and the semi-fused material, are used for other purposes. H. G. Greenish has described the manufacture of flowers of sulphur. L. N. Vauquelin said that sulphur purified by any of these methods may still retain arsenic sulphide, and bituminous matters, and it requires a number of fractional distillations to lower the proportion of these impurities. G. Osann said that half a dozen distillations give a product which sublimes without leaving a carbonaceous residue. G. S. Albright and J. J. Hood said that sulphur can be freed from organic matter by keeping it for a long time at a temp. in proximity to its b.p. The purification of sulphur was the subject of patents by F. Boude, A. Walter, E. Rasse-Courbet, E. F. J. Bert, A. A. Consoli, A. Dementieff, A. R. Scott and A. Meyer, the Société Anonyme Métallurgique, C. Marx, E. Legeler, etc. J. W. Schwab purified sulphur of a bad colour by melting it with finely-divided, active carbon.

The refined sulphur of commerce is of a high degree of purity. C. Mené found that the crude sulphur contained 88·7–96·2 per cent. of sulphur soluble in carbon disulphide and 1·5–2·1 per cent. insoluble in that menstruum; 0·5–1·1 per cent. of bituminous matters; 1·5–5·5 per cent. of sand, or silica; and 1·8–4·1 per cent. of alkaline earth sulphate. Flowers of sulphur may be contaminated with adsorbed sulphur dioxide which cannot all be removed by washing. H. Rössler found that while roll-sulphur is almost free from acids, flowers of sulphur may contain 3·142 c.c. of sulphur dioxide per 100 grms., and some sulphuric acid,

N. Leonhard observed an acidity eq. to 0·02–0·25 per cent. H_2SO_4. A. Harpf, W. Windisch, and N. Leonhard discussed the formation of this acid by sulphur when exposed to air. F. A. Flückiger said that some thiosulphuric acid is always present. Flowers of sulphur contains up to 33 per cent. of sulphur insoluble in carbon disulphide; and when first cast, H. St. C. Deville said that that roll-sulphur contains a certain proportion of amorphous sulphur and of sulphur insoluble in carbon disulphide; but this very gradually reverts to ordinary sulphur on keeping. This subject was discussed by A. Domergue, and E. Heckel. A. Payen showed that roll-sulphur, heated by itself, and flowers of sulphur, heated in contact with water, gave off hydrogen sulphide; but moist sulphur was found by A. Pleischl to give off the gas when heated. J. B. A. Dumas also showed that when sulphur enters into combination with the metals it may give off up to 0·1 per cent. of hydrogen; but if the sulphur has been previously fused, only a trace of hydrogen is evolved. Hence sulphur may contain hydrogen sulphide, or, as L. Prumer supposed, hydrogen persulphide, the hydrogen may come from organic matters, or water; or it may be occluded hydrogen.

Sulphur made from the spent oxide of gas-works is sometimes quite blackened with the so-called bituminous matters present. A. Peratoner found 0·03–2·44 per cent. of bitumen in ordinary crude Sicilian sulphur, and 5–8 per cent. in dark-coloured brimstone. R. V. Hasslinger observed that all the commercial sulphur he examined deposited on boiling a precipitate containing iron and carbon. Arsenic occurs in sulphur mainly as arsenic trisulphide; this may be partially oxidized as arsenic trioxide and, in exceptional cases, as calcium or ferric arsenite. This subject has been discussed by H. Hager, F. C. Steel, J. Brand, H. Schäppi, and H. S. and M. D. Davis. No arsenic was observed in sulphur from Texas. Sulphur, particularly that from Japan, may contain selenium. W. Smith found in Japanese sulphur, 0·3–0·8 per cent. As, and 0·045–0·152 per cent. Se. P. Klason found 1–2 grms. of selenium per ton of Japanese sulphur, and 0·9 grm. per ton in Sicilian sulphur. G. V. Brown also found selenium in sulphur from Sicily, Lipari, New Zealand, and Hawaii. Sulphur sometimes contains traces of tellurium. Sulphur at most contains 2 per cent. of ash, and F. Janda observed up to 0·283 per cent. of ash in 30 samples of commercial sulphur. E. Durier observed that in some cases the earthy matters present in ground sulphur are adulterants.

R. Threlfall and co-workers obtained sulphur of a high degree of purity by filtering molten sulphur through glass-wool, and then distilling it in vacuo. The product has no smell, and it can be evaporated or dissolved in carbon disulphide without residue.

The so-called *sublimed sulphur* is obtained from the collecting chamber. A. Domergue suggested that the term flowers of sulphur should not be applied unless the newly-made product contains not less than 33 per cent. of sulphur insoluble in carbon disulphide; if it contains less than this, it should be called sublimed sulphur. F. Diacon [10] graded sublimed sulphur into *grésil*, *éponges*, *grapillons*, and *candi*, according to its degree of fineness. The grésil is the finest grade, and is a pure sublimate collected at a distance from the vapour inlet tube, whilst the *candi* is the coarsest grade, and is collected near the vapour inlet tube. Much crude, or imported Sicilian or Louisiana sulphur is reduced to a fine powder by grinding—*ground sulphur*. It is graded by sifting. The finest grade obtained by pneumatic sifting or fanning is called *zolfo ventilato*. To avoid sparking and explosion during the grinding and sifting, A. Walter circulated an inert gas through the plant while in operation. H. Köhler recommended reducing the sulphur to a fine powder by dissolving it in its own weight of fused naphthalene, and removing the solvent by heat or extraction with a solvent. The so-called *plastic sulphur* of Imbert, for use in agriculture and viniculture, is not the viscous or plastic sulphur indicated in the next section, but is a mixture of sulphur with 0·05 per cent. of oxgall. The so-called *precipitated sulphur* of P. Kulisch is not the precipitated sulphur or milk of sulphur indicated below in connection with colloidal sulphur, but is a brown or black powder containing only 33 per cent. of real sulphur, and 50 per cent. of ferruginous ashes.

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§ 4. The Allotropic Forms of Sulphur

Several allotropic forms of sulphur have been reported, and these are characterized by differences in the crystalline form, sp. gr., solubility, etc. There is also the so-called amorphous sulphur, which, when really non-crystalline, may be regarded as colloidal sulphur. There are also two varieties of liquid sulphur. The general subject was discussed by M. Copisarow.[1] The varieties now called α-sulphur and β-sulphur were discovered by E. Mitscherlich in 1825—the former is the ordinary variety and furnishes octahedral crystals belonging to the rhombic system, and the latter prismatic crystals belonging to the monoclinic system. Natural sulphur, and sulphur crystallized from carbon disulphide, chloroform, bromoform—or, according to P. Gaubert, acetylene tetrabromide—or other solvents at not too high a temp., furnishes **rhombic, octahedral, or α-sulphur,** or **Muthmann's sulphur I**. C. Brame, P. Schützenberger, L. Bombicci, O. Silvestri, and G. vom Rath obtained rhombic crystals from the molten magma ; R. Brauns said that it is easiest to obtain the rhombic form from molten sulphur by seeding the undercooled liquid with a rhombic crystal ; and J. H. L. Vogt said that the free sulphur in slags always occurs in association with the cubic monosulphides. A. Daubrée observed this form of sulphur in some cracks in the masonry of the burner of a sulphuric acid works at Strassburg, in which sulphur was melted at a temp. of about 80° ; A. Arzruni found some in a mine at Zielenzig, Brandenburg ; G. Leonhard, and P. Groth, from a gob-fire in the coal-shales of Duttweiler, Saarbrücken ; and F. Ulrich, and A. Brezina, from a furnace at Oker, Harz. The crystals in both cases are supposed to have been produced by sublimation. H. Erdmann observed some rhombic crystals were formed in a vessel in which alcohol and a dye containing sulphur has been kept for twenty years. According to L. Ilsovay de Nagy Ilosva, if the sulphur crystallizes at a temp. over 120°, it appears in the prismatic, monoclinic form, and below 120°, in the rhombic, octahedral form. M. Spica treated calcium polysulphide with hydrochloric acid and dissolved the white precipitate in ether and obtained crystals which L. Maquenne said are really rhombic although they have the prismatic form. P. Hautefeuille obtained rhombic crystals of sulphur by repeatedly heating and cooling a mixture of sulphur and conc. hydriodic acid in a sealed tube. F. B. Ahrens observed that the slow oxidation of hydrogen sulphide dissolved in pyridine or picoline furnished rhombic crystals of sulphur. W. Spring observed that monoclinic sulphur passes into the rhombic form under a press. of 5000 atm.; and J. W. Judd, and R. Threlfall obtained a similar result from amorphous sulphur at a press. of 6000 atm. F. Köhler studied the rhythmic crystallization of sulphur.

J. B. L. Romé de l'Isle,[2] in 1783, found that the crystals, obtained by cooling molten sulphur, occur *en aiguilles fines, divergentes, et rhomboidales*. According to E. Mitscherlich, **prismatic, monoclinic, or β-sulphur**—or **Muthmann's sulphur II**—is formed if, say, 500 grms. of sulphur be melted in a clay or porcelain crucible and the mass allowed to stand until a surface crust is formed. Long, prismatic, needle-like crystals of wax-yellow sulphur will be found to have grown on the walls of the crucible, and on the underside of the crust when the crust is pierced, and the still fluid sulphur is poured away. Hot sat. soln. of sulphur in alcohol, ether, and benzene were found by C. J. St. C. Deville to give this form of sulphur; A. G. Bloxam obtained it from soln. in alcohol; E. Royer, and W. Muthmann, from soln. in hot turpentine; and P. Gaubert, in acetylene tetrabromide. The variety obtained by W. Muthmann by exposing in air an alcoholic soln. of ammonium sulphide was at first thought to be β-sulphur, but later, was found to be another variety—δ-sulphur. M. L. Frankenheim said that this form of sulphur is produced by sublimation or precipitation at a temp. near the m.p. of sulphur—L. Ilsovay de Nagy Ilosva said above 120°. O. Silvestri, A. Oglialoro-Todaro, and P. Groth stated that this form of sulphur may occur as stalactites in the craters of volcanoes; and that it is very quickly transformed into the rhombic variety. W. Haidinger applied the term **sulfurite** to the monoclinic form of sulphur regarded as a mineral. According to W. Muthmann, some of the prismatic sulphur described by previous investigators is really a different variety of prismatic sulphur. Roll-sulphur when freshly cast was found by C. J. Fritzsche to be β-sulphur; and this soon changes to α-sulphur. Under the microscope, flowers of sulphur has the appearance of smooth, opaque spherules with a non-crystalline fracture. The minute drops, condensed from sulphur vapour on a glass plate, may remain liquid for days if left at rest, and they finally solidify to form smooth globules; if the drops are agitated, or exposed to light, they solidify in a few hours by spreading themselves on the glass plate in the form of opaque hemispheres with crystalline points of rhombic-octahedra. If the glass plate be wetted with oil, the crystals are larger and are more quickly formed. L. Frischauer found that drops with a diameter below 30μ do not crystallize spontaneously, while those over 180μ crystallize in a few minutes. β-rays hasten the crystallization of under-cooled sulphur. R. Brauns found that the metastable monoclinic sulphur can be kept unchanged for years between a microscopic slide and cover-glass.

L. Pasteur said that monoclinic crystals can be obtained at ordinary temp. from soln. of sulphur in carbon disulphide; S. Barilari obtained the crystals of the same form by the spontaneous evaporation of a soln. of sulphur in a mixture of alcohol and ammonium sulphide; while D. Gernez found that a supersaturated soln. of sulphur furnishes either rhombic or monoclinic sulphur, or both forms simultaneously, if the soln. be seeded with a fragment of the desired form. E. Royer said that if a hot sat. soln. of sulphur in turpentine be rapidly cooled, monoclinic sulphur is formed, and if slowly cooled, rhombic sulphur is produced. In repeating this experiment, W. Muthmann found that only the β-form was produced, if more sulphur was present than the turpentine (at 150°) could dissolve. C. J. St. C. Deville found that alcoholic soln. give both forms of sulphur; while benzene soln. furnish first the β- and then the α-forms. H. J. Debray observed that when a mixture of sulphur and carbon disulphide (2 : 1) is heated in a glass tube to 80°, and rapidly cooled, there are produced prisms of the β-form which quickly pass to the α-form.

According to E. Mitscherlich, α-sulphur passes into the β-form in the proximity of its m.p.; B. C. Brodie said between 100° and 114·5°. L. T. Reicher gave 95·6° for the transition temp.; D. Gernez, 97·6°; G. Tammann, 94·6°. R. F. Marchand and T. Scheerer found that the crystals of β-sulphur, when kept a few days at ordinary temp. show isolated bright yellow, opaque spots which gradually spread themselves out so that the mass becomes bright yellow, opaque, and specifically heavier owing to the formation of α-sulphur—the crystals are pseudomorphs after β-sulphur. The change is accompanied by the formation of internal fissures. If α-sulphur be kept some days at 100°–110° it becomes specifically lighter, but the former sp. gr. is restored when it is kept at ordinary temp. a few days. The change is a case of *enantiotropic allotropy*—*ἐναντίος*, opposite; *τρόπος*, habit—for, as L. T. Reicher showed, it is reversible; above or below the transition temp. only one of the two forms is stable and the other unstable. According to D. Gernez, α-sulphur does not pass into the β-form if heated below its m.p., and yet above the transition temp., the transition occurs only when a trace of β-sulphur is present. When the transformation is suspended beyond its transition point, the sulphur is in a state of what D. Gernez, and E. Mallard called *la surfusion cristalline.* The passage from α- to β-sulphur can be detected at about 97·5°, but it varies with the source from which the sulphur is obtained, and P. Duhem showed that it depends on the proportion of soluble and insoluble sulphur present—it rises with an increasing proportion of insoluble sulphur—and it also depends on other physical conditions. C. J. St. C. Deville observed that at a low temp., unstable monoclinic sulphur is but slowly transformed into stable rhombic sulphur. This subject was discussed by E. Cohen. D. Gernez measured the effect of temp. on the rate of transformation of α- to β-sulphur between 97·5° and the m.p., and of β- to α-sulphur from 95·1° to —23°. The results in the latter case are shown graphically in Fig. 5. R. Brauns, L. T. Reicher, and P. Duhem also showed that the effect is dependent on the temp. J. M. Ruys observed that the transformation of a given mass occupied twelve days between —36° and —15°, and ten days between —31° and —5°. The subject was investigated by S. L. Bigelow and E. A. Rykenboer. W. Fränkel and W. Goez assumed that the transformation originates at a number of points and spreads outwards, with a constant linear velocity at a constant temp., the amount of transformation of monoclinic to rhombic sulphur at temp. a little above the ordinary temp., and for rhombic to monoclinic sulphur at 100°, in unit time, increases with the square of the time until the boundaries of the changed areas meet, the transformation velocity is then constant, and finally diminishes. The curve for the total amount of transformation thus rises at first with the third power of the time, it then gradually flattens, and then falls. For supercooled monoclinic sulphur, the maximum rate of transformation to rhombic sulphur occurs at —20°. C. Montemartini and L. Losana measured the rate of conversion from one form to another by means of an automatic recording apparatus; W. Flörke described demonstration experiments on the subject.

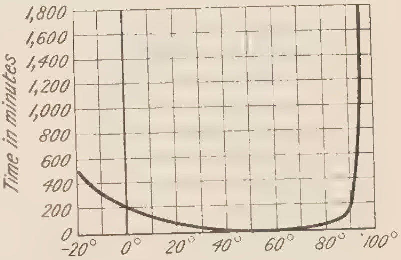

FIG. 5.—The Effect of Temperature on the Rate of Transformation of β- to α-Sulphur.

P. Duhem said that β-sulphur which has been kept for some time below the transition temp. furnishes α-sulphur which has a rate of transformation to β-sulphur different from that which is obtained with ordinary sulphur. R. Threlfall and co-workers also said that α-sulphur obtained from β-sulphur is different from that which is obtained in the ordinary way. As indicated above, this is connected with the different proportions of the soluble and insoluble sulphur present in the mixture. The transformation of β- to α-sulphur is accelerated by the presence of α-sulphur, by contact with carbon disulphide and other solvents, and, according to

E. Mitscherlich, "by the slightest agitation, even blowing on the crystals." C. Brame also noticed that the transformation is accelerated by the chemically active rays of light. The effect of press. was found by L. T. Reicher to be such that the transition point is raised 0·05° per atm.; and G. Tammann found that at higher press., p kgrms. per sq. cm.,

p	1	123	391	638	873	1108	1350
Transition temp.	94·6°	100·11°	110·11°	120·01°	129·91°	140·1°	150·1°

At 1320 kgrms. per sq. cm., and 150·1°, there is a triple point in which α- and β-sulphur are in equilibrium with molten sulphur—O_3, Fig. 6. H. W. B. Roozeboom calculated 400 atm. press., and 131° for the triple point. Curve PO_1, Fig. 6, is obtained by plotting the vap. press. of rhombic sulphur at different temp.; similarly, the curve O_1O_2 is obtained by plotting the vap. press. curve of monoclinic sulphur, this variety of sulphur melts at 120°; O_2Q is obtained by continuing the vap. press. curve of the liquid; the curve O_1O_3 by plotting the transition points of rhombic sulphur at different press.; and the curve O_2O_3, by plotting the m.p. of monoclinic sulphur at different press. The curves are exaggerated in the diagram. Monoclinic sulphur cannot exist in a stable state at press. higher than that represented by the point O_3. The continuation of the curve O_3N represents the effect of press. on the m.p. of rhombic sulphur. In Fig. 6, there is the additional complication corresponding with the two forms of sulphur now under consideration. The phase rule enables a very clear idea of the conditions of equilibrium to be formed. There are here only one component sulphur, and four possible phases—sulphur vapour and liquid, and rhombic and monoclinic sulphur. When the condition of the system is represented by a press. and temp. corresponding with one of the three triple points—O_1, O_2, and O_3—the system is univariant, and any change in temp. or press. will lead to the suppression of one of the three phases; points on one of the curves—PO_1, O_1O_2, O_2Q, etc.—represent a univariant system; and points in one of the three regions—PQ, QO_2N, NO_1P—represent a bivariant system. Can all four phases exist under any conditions of temp. and press. in a state of equilibrium? According to the phase rule, the variance of such a system will be $1-4+2=-1$. This is an impossible value. Such a system would not be in a state of true equilibrium. The metastable states are interesting. The curves QO_2 and the PO_1 meet at a point corresponding with 114·5°. This is the m.p. of rhombic sulphur. If the transformation of rhombic to monoclinic were very fast, it would be impossible to state the m.p. of rhombic sulphur, because it would pass into the monoclinic form before a determination could be made. The upward left-to-right slopes of the curves NO_3 and O_1O_3 correspond with the fact that the m.p. of sulphur is raised by increasing press. The converse is true in the case of ice, and in consequence, the corresponding curve with ice slopes the opposite way.

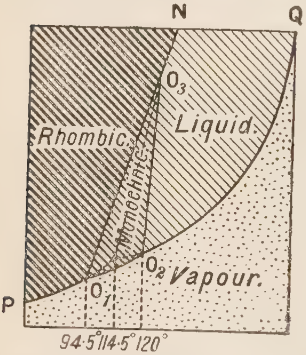

Fig. 6.—Vapour Pressure of Sulphur (Diagrammatic).

D. Gernez[3] recognized another variety of sulphur which he called *soufre nacré*. It was, however, probably obtained before D. Gernez's time. D. Gernez obtained γ-sulphur mixed with some α- and β-sulphur from crystallizing molten sulphur—melted at 150° and cooled to 90°—when crystallization is initiated by rubbing the walls of the glass containing vessel with a glass rod or a platinum wire. R. Brauns obtained nacreous sulphur by cooling a drop of molten sulphur at a temp. exceeding 120° on a glass microscopic slide; and P. Gaubert also obtained it from drops of under-cooled liquid sulphur at ordinary temp. W. Salomon supposed that the crystals obtained by O. Bütschli from drops of under-cooled sulphur sublimed on to a glass-slip, were γ-sulphur. W. Muthmann thought that the labile sulphur obtained by O. Lehmann from molten sulphur might be γ- or δ-sulphur. P. Groth supposed it to be γ-sulphur. It is formed when sulphur is produced by certain chemical reaction; for instance, by the slow diffusion of aq. soln. of sodium thiosulphate and potassium hydrosulphate. The yellowish-white crystals have a mother-of-pearl lustre, and they are monoclinic with axial ratios different from those of β-sulphur—*vide infra.* This variety of sulphur is called **nacreous sulphur, γ-sulphur,** or **Muthmann's sulphur III.** It may be noted that the term γ-sulphur was also applied to a colloidal or amorphous sulphur insoluble in water and in carbon disulphide, but the time is ready for another enumeration. Similar crystals were made by E. Mitscherlich by saturating an alcoholic soln. of sodium sulphide with sulphur; filtering off the clear reddish-coloured supernatant liquid, and, after adding a little more alcohol, letting the soln. stand for some time. Needle-like crystals of nacreous sulphur grow from the surface of the soln. M. Spica obtained this form by treating calcium polysulphide with hydrochloric acid; and the amorphous sulphur, soluble in carbon disulphide, obtained by M. Berthelot by treating alkali thiosulphates with hydrochloric acid, was probably this variety. Similarly also S. Cloez obtained this form by the slow decomposition of sulphur monochloride or monobromide in moist air. The product quickly passes into α-sulphur by contact with the liquid monochloride, and W. Muthmann found it better to leave a beaker of sulphur monochloride and one of methyl alcohol standing under a clock glass in a warm place. H. W. Kohlschütter discussed the transformation to rhombic sulphur. P. Sabatier, L. Maquenne, and J. H. Walton and L. B. Parsons obtained similar crystals by treating hydrogen disulphide with alcohol, ether, or ethyl acetate, and also by adding ether to a soln. of sulphur in carbon disulphide. Nacreous sulphur was also prepared by D. Gernez in the following manner: Heat sulphur in a sealed tube with benzene, or toluene, carbon disulphide, alcohol, etc., so that there is no undissolved sulphur in the tube when the tube is hot. Then immerse one end of the tube in a freezing mixture formed, say, by dissolving ammonium nitrate in cold water. Long, nacreous flakes separate at the cold end of the tube and gradually extend into the remaining soln.

A number of reports is not so clear. A. Payen obtained from a hot sat. soln. of sulphur in alcohol, benzene, turpentine, or olive oil, prismatic crystals of what was probably β-sulphur, and tabular crystals of γ-sulphur; C. J. St. C. Deville obtained similar crystals by cooling between 75° and 80° a soln. of sulphur in chloroform, alcohol, ether, or benzene—some α-sulphur appears at 23° or 24°, and below 22°, according to W. Muthmann, all is α-sulphur. Only crystals of γ-sulphur are formed by heating a soln. of sulphur in benzene in a sealed tube at 140°. By rapidly cooling a hot, sat. carbon disulphide soln. of sulphur in a sealed tube, H. J. Debray obtained only α-sulphur; and D. Gernez, using carbon disulphide, benzene, or toluene as solvents, obtained γ-sulphur. E. Royer obtained α-sulphur by slowly cooling a hot sat. soln. of sulphur in terpentine; and β-sulphur, by slowly cooling the soln. If boiling turpentine be treated with more sulphur than it can dissolve, and a drop of the soln., sat. at 150°, be placed on the object glass of a microscope and rapidly cooled, W. Muthmann said that only γ-sulphur is formed. M. H. Deschamps, C. L. Bloxam, C. M. Wetherill, and S. Barilari also reported forms of sulphur—probably γ-sulphur—obtained from hot alcoholic soln.

A fourth modification of sulphur, also monoclinic, is sometimes called **tabular sulphur,** and also **Muthmann's sulphur IV**, or **δ-sulphur**—the old δ-sulphur is a colloidal form soluble in both carbon disulphide, and water. It is obtained in thin tabular crystals, mixed with some γ-sulphur, from a soln. of sulphur in an alcoholic soln. of ammonium sulphide cooled to 5°. This form passes so readily into the α-form that the crystals have not been accurately measured.

A fifth variety of sulphur, also called **rhombohedral or trigonal sulphur,** or **ϵ-sulphur,** was obtained by R. Engel by pouring, with continual stirring, one vol. of a soln. of sodium thiosulphate, sat. at ordinary temp., into 2 vols. of a soln. of hydrochloric acid, sat. at 25°–30°, and cooling the mixture to about 10°. Sodium chloride is precipitated, and the thiosulphuric acid is so far stable that the liquid can be filtered. The filtrate is at first colourless, but soon becomes yellow, the intensity of the colour gradually increasing, as if a soluble sulphur establishes equilibrium in the decomposition of the thiosulphuric acid; sulphur dioxide is evolved at the same time. When the liquid has acquired a deep-yellow colour, but while it is still quite transparent, it is agitated with its own vol. of chloroform, which becomes yellow, whilst the colour of the aq. soln. becomes less intense. If the chloroform is allowed to evaporate, orange-yellow crystals of sulphur are obtained, quite different from octahedral sulphur. C. Friedel said that the orange-yellow crystals are trigonal, and, with converging polarized light, they show the cross and rings of birefringent, uniaxial substances. Tellurium and selenium also crystallize in the trigonal form. R. Engel added that the crystals are denser than octahedral sulphur (sp. gr.=2·135), and at first are transparent, but in three or four hours they increase in volume, and pass gradually into the state of amorphous, insoluble sulphur. They melt below 100°, and pass into the condition of the pasty sulphur from the thiosulphates and become partially soluble in carbon disulphide.

C. Friedel reported another form—*triclinic sulphur* or *ξ-sulphur*—which collected as a sublimate in the upper part of a sulphur vapour bath. The crystals were said to be very unstable and to pass rapidly into α-sulphur. These observations have not been verified.

According to G. Linck and E. Korinth, if a soln. of sulphur in carbon disulphide be thickened with rubber or Canada balsam, and allowed to evaporate, the sulphur first appears as a cloud of globulites about 1μ in diameter. Some of these increase in size at the expense of their neighbours. When a crystal is formed it grows in the same way, the drops in the vicinity moving towards it being carried by the stream of the more conc. soln. to the crystal. An unstable, pale yellow, tetragonal form, or **θ-sulphur,** appears in the soln. E. Korinth also observed the same variety to be formed from a chloroform soln. of sulphur thickened with rubber, and mixed with a few drops of benzonitrile. This unstable form rapidly passes into what appears to be W. Muthmann's δ-sulphur. Another variety of sulphur, **ζ-sulphur,** was obtained from this soln. It forms colourless, rhombic plates which have a weak double refraction. There is also formed a variety, **η-sulphur,** which furnishes colourless, doubly refracting, hexagonal plates. Both the ζ- and η-forms are more stable than δ-sulphur. Excluding the trigonal ε-sulphur, and the triclinic ξ-sulphur, the stability and transformations of the other varieties are thought by E. Korinth to follow the sequence of changes:

$$\theta\text{-tetragonal}\rightarrow\delta\text{-monoclinic}\rightarrow\eta\text{-monoclinic}\rightarrow\zeta\text{-monoclinic}\rightarrow$$
$$\rightarrow\gamma\text{-monoclinic}\rightarrow\beta\text{-monoclinic}\rightleftharpoons\alpha\text{-rhombic.}$$

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§ 5. Amorphous and Colloidal Sulphur

A number of varieties of sulphur have in the past been classed as **amorphous sulphur.** The *lac sulphuris*, prepared by Geber,[1] G. E. Stahl, C. W. Scheele, and T. Bergman, is an example of one kind. A. F. de Fourcroy and M. de la Porte observed that *l'eau sulfureuse d'Enghien* has *un' odeur hepatique*, and when oxidized, it becomes turbid. The suspended sulphur is not removed by filtration for *la liqueur passoit trouble et laiteuse à travers deux papiers.* The liquor is *très-transparente*, and *d'une couleur légèment citrine.* C. L. Berthollet added : *par l'addition d'un sel, tel que le muriate de soude le précipité se formoit promptement et la liqueur restoit claire.* Analogous observations with respect to the sulphur produced by the oxidation of a soln. of hydrogen sulphide were made by M. le Veillard, J. J. Berzelius, J. W. Döbereiner, J. Persoz, J. Dalton, etc. M. Berthelot reported a variety soluble in carbon disulphide to be formed by the action of hydrochloric or sulphuric acid on alkali or alkaline earth polysulphides, by the spontaneous

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decomposition of hydrogen polysulphide, and by the slow oxidation of a soln. of hydrogen sulphide in air. If the polysulphides are oxidized by ferric chloride, nitric acid, etc., part of the sulphur is insoluble in carbon disulphide. H. R. Brownlee showed that when a soln. of calcium or sodium polysulphide is treated with conc. hydrochloric acid, the precipitate contains a small proportion of insoluble sulphur, but with acetic or dil. hydrochloric acid, insoluble sulphur is not produced. It is found that the so-called "soluble" or "soft, amorphous sulphur" precipitated from polysulphides is not amorphous, but crystalline. D. Gernez, and E. Petersen consider that this form of sulphur is not essentially different from ordinary sulphur; and W. Muthmann, that the crystals first formed are γ-sulphur. S. Cloez thought that sulphur precipitated from acid or alkaline soln. was respectively soluble or insoluble; but H. R. Brownlee showed that freshly precipitated sulphur consists entirely of insoluble sulphur and that the reversion to soluble sulphur is retarded by the contact action of the acid or halogen in the liquid. The proportion of insoluble sulphur which overcomes this tendency to revert depends on the concentration of the acid or halogen employed.

The so-called *milk of sulphur*, or *lac sulphuris*, is obtained from cold aq. soln. containing hydrogen sulphide—*e.g.* C. F. Bucholz, and H. W. F. Wackenroder used aq. soln. of a preparation containing alkali or alkaline earth polysulphide. One of these liquids is allowed to stand a few days, filtered, diluted with water, and the sulphur precipitated by adding sulphuric, hydrochloric, or acetic acid in small portions at a time with constant stirring. If acid be added in excess, ordinary yellow sulphur will be precipitated along with the white or grey milk of sulphur. T. Thomson thought that milk of sulphur is hydrated, but C. F. Bucholz, and G. Bischof found that this is not the case. W. Spring, however, regarded colloidal sulphur as a hydrate $S_8.H_2O$. J. J. Berzelius found that some hydrogen sulphide, not water, is given off in drying; and H. Rose inferred that milk of sulphur is a compound of sulphur and hydrogen sulphide or polysulphide because the amount evolved on drying is constant; the polysulphide cannot be removed by washing; and milk of sulphur is formed only from liquids containing hydrogen sulphide. H. Rössler observed that milk of sulphur always contains some thiosulphuric acid; L. Prunier, some hydrogen polysulphide, which is gradually decomposed by washing; and G. Osann, some admixed carbon.

Another form of amorphous sulphur is said to be a variety insoluble in carbon disulphide; it is converted into the insoluble form by repeated dissolution in carbon disulphide and evaporation. C. J. St. C. Deville, R. Weber, M. Berthelot, and F. Selmi and G. Missaghi found that it is formed along with an insoluble form by many of the methods indicated below. G. Magnus and R. Weber obtained it by strongly heating and rapidly cooling ordinary sulphur, and extracting with carbon disulphide. The α-sulphur crystallizes out first, and there remains this variety in a form which they called *krümligen Schwefel*. It is doubtful if this is a specific variety; rather is it a mixture of sulphur soluble and insoluble in carbon disulphide.

There is a variety of amorphous sulphur which is insoluble in carbon disulphide, and which has been called γ-*sulphur*, but that term is here used for a variety of crystalline sulphur. The varieties of so-called amorphous sulphur just indicated, as being soluble in that menstruum, are probably not specific individuals, but rather mixtures of two or more other varieties. The insoluble, amorphous sulphur is generally regarded as being the μ-form of sulphur discussed below; and soluble, amorphous sulphur as the λ-form. In all the methods of making insoluble, amorphous sulphur, some soluble sulphur is formed at the same time, and this is removed by extraction with carbon disulphide, leaving insoluble, amorphous sulphur as a residue. This variety is produced in numerous ways. It was prepared by E. Mitscherlich,[2] G. Osann, C. J. St. C. Deville, B. C. Brodie, R. F. Marchand and T. Scheerer, E. Petersen, B. Rathke, M. Töpler, and A. Smith and W. B. Holmes by pouring sulphur, melted at a high temp., into cold water, and, after some days, extracting the product with carbon disulphide. A. Lallemand obtained it by exposing a conc. soln. of sulphur in carbon disulphide to sunlight; M. Berthelot found that the electric light acted in the same way, and that hydrogen sulphide in the soln. retards the change. Solid sulphur in sunlight does not suffer this change. Some insoluble, amorphous sulphur is formed when sulphur vapour is condensed in air, and flowers of sulphur, as previously indicated, contains some of this variety. The reaction was examined by C. J. St. C. Deville, and M. Berthelot. As shown by F. Selmi, F. Sestini, W. Müller, C. F. Cross and A. F. Higgin, and M. Berthelot, it is formed when sulphur vapour is condensed in water or in steam; and, according to J. Gal, when sulphur vapour is condensed on the surface of a cold liquid such as water, dil. nitric acid, dil. hydrochloric acid, or a soln. of sodium hydroxide, plastic sulphur is formed in thin pale-yellow plates which under the microscope are seen to be formed of transparent, rounded grains. The plates consist of a mixture of soluble and insoluble sulphur; if heated at 100° for an hour, 13·6 per cent. remains insoluble in place of the 0·3 per cent. in the case of ordinary plastic sulphur, and 23 per cent. in the case of flowers of sulphur. The proportion of insoluble sulphur in plastic sulphur formed from vapour varies with the conditions, and especially with the temp. of vaporization. The percentages of insoluble sulphur at various temp. above 200° are:

	215°	230°	245°	260°	275°	290°	305°	320°
Insol. Sol .	18	22	25	28	31	34	36	37

Water, nitric and hydrochloric acids, and soln. of sodium and potassium hydroxides and sulphurous acid at 0° give practically the same result, the product containing 45 per cent. of insoluble sulphur. With sulphuric acid, the proportion of insoluble sulphur is as high as 75 per cent., whilst with ammonia it is as low as 15 per cent. In the last case the product is not soft, but forms brittle plates. There is, however, no relation between the elasticity of the product and the proportion of insoluble sulphur that it contains; the sulphur condensed on the surface of a block of ice is very elastic, but only 20 per cent. of it is insoluble. For one and the same condensing liquid, the proportion of insoluble sulphur is higher the higher the temp. of the sulphur vapour. With sulphuric acid and sulphur vapour at 300°, a variation in the temp. of the acid between 0° and 160° has no influence on the insolubility of the product. With sulphur vapour at 440° and sulphuric acid, or with sulphur vapour at 300° or 440° and water, or liquid sulphur at 440° and water, the proportion of insoluble sulphur in the product is higher the lower the temp. of the condensing liquid. If the flame of hydrogen sulphide or carbon bisulphide is allowed to impinge on the surface of a cold liquid, the hydrogen or carbon burns before the sulphur, and the latter is condensed in a plastic condition. M. Berthelot obtained insoluble amorphous sulphur by the action of, say, 15–20 vols. of water on sulphur monochloride or bromide frequently shaken for about six days—E. Petersen used a dil. soln. of sodium carbonate. M. Berthelot decomposed thiocarbonyl dichloride with a dil. soln. of sodium carbonate; and by extracting the so-called sulphur monoiodide with carbon disulphide either at ordinary temp., or at 80°–100°. M. J. Fordos and A. Gélis, and M. Berthelot obtained this form of sulphur by the action of hydrochloric acid on a soln. of sodium thiosulphate; and M. Berthelot also used sulphuric and sulphurous acids. M. Berthelot also obtained this form of sulphur by the action of an acid on potassium trithionate, sodium tetrathionate, or pentathionic acid; by the electrolysis of sulphurous acid, and by heating sulphuric acid to 160°–180° in a sealed tube; H. W. F. Wackenroder, A. Sobrero and F. Selmi, M. J. Fordos and A. Gélis, S. de Luca and J. Ubaldini, and M. Berthelot, by the action of hydrogen sulphide on sulphurous acid; M. Berthelot, by the action of sulphur dioxide on soln. of alkali sulphides; and by the electrolysis of conc. sulphuric acid or by the action of hydrogen sulphide or phosphine on that acid. E. Münster, and E. Mulder obtained it by the action of hydrogen sulphide on fuming nitric acid; W. R. E. Hodgkinson, by the action of hydrogen sulphide on chlorine, bromine, or iodine; and F. Selmi, on nitrogen tetroxide, nitric acid, aqua regia, and soln. of ferric salts; F. Selmi and G. Missagi, on sulphur monochloride; and M. Berthelot, on chromic acid. P. Sabatier obtained it by the action of a sat. soln. of hydrogen sulphide on hydrogen polysulphide, and M. Berthelot, by the action of fuming nitric acid on metal sulphides. Nitric acid, or sulphur dioxide, acts on molten sulphur above 115°, forming some insoluble, amorphous sulphur. M. Dietzenbacher found that by heating 400 parts of sulphur with one part of iodine or potassium iodide much insoluble sulphur is produced; bromine acts at 200°, and chlorine at 240°, producing respectively 75–80 per cent. and 65–70 per cent. of insoluble sulphur. According to A. Wigand, when liquid or dissolved sulphur—with benzene or carbon tetrachloride as solvents—is exposed to light, the insoluble sulphur which separates—S_μ—is in the colloidal state. The change of soluble sulphur—$S\lambda$—into insoluble sulphur on exposure to light is reversible, and a true photochemical equilibrium is attained, both in the case of liquid and dissolved sulphur. The position of equilibrium and the rate of change depend on a number of factors, such as the temp., rate of stirring, nature of solvent, extent of surface exposed to light, etc. J. Amann found that under the influence of light, soln. of sulphur in carbon disulphide, carbon tetrachloride, benzene, amyl alcohol, or turpentine, show considerable changes in the ultramicroscopic character of the solutions. The transition from the amicroscopic to the micellary condition diminishes in velocity as the viscosity of the dispersive medium increases. The adsorption of the particles by the glass walls of the containing vessel decreases simultaneously.

According to K. Schaum, all kinds of sulphur, which are insoluble in carbon disulphide, are amorphous, and when pure furnish flocculent powders. M. Berthelot found that these forms of sulphur very slowly pass into the α-form, for flowers of sulphur which has been kept 50 years still contains some insoluble sulphur. The change to the stable α-form is rapid with this and all other varieties of sulphur when heated above the m.p. and slowly cooled; and if heated to 110°–120° for some weeks in contact with soln. of alkalies, alkali sulphides, or hydrogen sulphide. C. J. St. C. Deville found that insoluble sulphur is very slowly transformed into soluble sulphur at 60°–70°; and A. Smith and W. B. Holmes observed that a sample with 2·8 per cent. of insoluble sulphur when kept 10 hrs. at 70°, contained only 0·57 per cent., and none when treated similarly at 100°. M. J. Fordos and A. Gélis, G. Magnus, M. Berthelot, B. C. Brodie, and R. Weber also noticed that the transformation readily occurs in contact with water at 100° or by simply heating the insoluble sulphur to that temp. M. Berthelot said that the insoluble sulphur prepared from thiosulphates is least stable towards heat, and passes into soluble α-sulphur most rapidly. At first, the transformation with the insoluble variety of sulphur prepared from sulphur monochloride proceeds more quickly than is the case with that obtained from flowers of sulphur; but after 15 minutes, the transformation with the variety obtained from sulphur monochloride proceeds most slowly. M. Berthelot found that contact with iodine, sulphur monochloride or bromide, or with fuming nitric acid, favours the transformation of the less stable insoluble form into the more stable α- or soluble form. K. Schaum, and A. Smith and W. B. Holmes observed that contact with carbon disulphide favours the transformation of insoluble into soluble sulphur. K. Schaum supposed that there is a state of equilibrium between the two forms in the presence of carbon disulphide as is shown by the passage of α-sulphur into the insoluble form by exposure to light. According to F. W. Küster, when soluble sulphur is heated in vacuo at 141·7°, about 5·2 per cent. of insoluble sulphur is formed, the amount formed being independent of the time; after 1 hour, this amount is approximately the same as after 16 hours. When heated at 183°, the amount of insoluble sulphur is also independent of the time, and also apparently of the temp., since about 6 per cent. of insoluble sulphur was obtained. When heated at 448° for 15 minutes and then gradually cooled, 1·8 to 3·3 per cent. of insoluble sulphur is formed; when, however, the molten sulphur is suddenly cooled by plunging into cold water, 30·9 to 34·2 per cent. of insoluble sulphur is obtained. The formation of the insoluble modification and the converse formation of soluble sulphur take place, therefore, with extreme rapidity, so that the amount of insoluble sulphur which is present after crystallization is not dependent on the temp. and time of the heating, but on the rate of the crystallization and the temp. at which it takes place. A sample of insoluble sulphur which has been kept for 5 months, when treated with carbon bisulphide, gives the same percentage of soluble matter as when freshly prepared. On evaporating the solution, the sulphur separates in solid drops which show no signs of crystallization under the microscope, but give evidence of crystallization when subjected to polarized light. This sulphur is not completely soluble in carbon bisulphide, so that the "insoluble" modification, when dissolved, is not completely converted into the soluble modification. Hence, it is concluded that the soluble and insoluble modifications have different molecules in soln., that they are not only physical isomerides, but chemical isomerides, having a relation to each other similar to that of ozone to oxygen. According to W. Spring, at 8000 atm. press., the insoluble part of flowers of sulphur passes into the α-form at 13°; R. Threlfall and co-workers also noticed that when the insoluble form of sulphur is subject to press., it passes into the soluble form. L. Troost and P. Hautefeuille found the sp. gr. of soluble sulphur to be 2·046; E. Petersen, 1·87; R. F. Marchand and F. Scheerer, 1·957–1·961; C. J. St. C. Deville, 1·919–1·928; B. Rathke, 1·91–1·93; G. Osann, 2·027; and M. Töpler, 1·849 at 40°–50°. M. Töpler also found that if the sp. vol. of liquid sulphur at 120° is unity that of insoluble sulphur at 30° is 0·963; at 60°, 0·979; at 120°, 0·995; at 140°, 1·001; at 160°, 1·007; at 180°, 1·014; and at 200°, 1·021. The coeff. of thermal expansion is 0·0003–0·0004 at 30°. M. Berthelot observed that the passage from the insoluble to the soluble form is attended by a rise of temp., and that this is due to the insoluble sulphur possessing a greater sp. ht. than α-sulphur. The heats of oxidation of both forms is 69·1 Cals. E. Petersen gave 71·99 Cals. for the insoluble amorphous form, and 71·99 Cals. for ordinary α-sulphur. P. A. Favre showed that the heat of oxidation of insoluble sulphur to sulphuric acid is less than is the case with α-sulphur; and is such that an eq. of α-sulphur develops 2102 cals. in passing to insoluble sulphur; while the passage of an eq. of oily sulphur from thiosulphate develops 3102 cals. in passing to insoluble amorphous sulphur. P. A. Favre and J. T. Silbermann found that sulphur recently melted and crystallized has a higher heat of oxidation than that which has been crystallized for a long time.

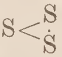
M. Berthelot assumes that the sulphur present in different compounds is in a different state—*e.g.* the sulphur in the alkali polysulphides is said to be present in the soluble form; whilst in the thiosulphates and sulphur monochloride, it is in the insoluble state; and that sulphur is soluble when present as an electronegative element, and insoluble when electropositive. He considers that this is shown by the modes of formation of the different varieties of sulphur, as well as by the electrolysis of an aq. soln. of hydrogen sulphide where only soluble sulphur appears on the positive pole; and in the electrolysis of sulphurous acid, almost insoluble sulphur collects on the negative pole. The soluble sulphur is said to unite more readily with the metals than does insoluble sulphur, but P. A. Favre found that the insoluble sulphur is oxidized more readily by hypochlorous acid than α-sulphur. S. Cloez does not agree with M. Berthelot since he found that insoluble sulphur unites more readily with iron and mercury, and with nascent hydrogen produces more hydrogen sulphide than does soluble sulphur. He supposed that sulphur separates from all compounds in the insoluble form, and that it is transformed by the surrounding liquid into more or less soluble sulphur. L. Faucher found that when flowers of sulphur is boiled with a soln. of sodium hydrosulphite, the insoluble form of sulphur is the first to dissolve; F. Bellamy also found that the insoluble form of sulphur gives more hydrogen sulphide when boiled with a soln. of sodium sulphite and it is dissolved more quickly. W. Schmitz-Dumont said that both kinds of sulphur give the same amount of hydrogen sulphide, but the insoluble form does dissolve more quickly. W. Müller-Erzbach showed that insoluble sulphur is oxidized by potassium permanganate more quickly than is the soluble form; and M. Berthelot, that the insoluble sulphur is more active in forming trithionic acid than is the case with α-sulphur.

A variety of sulphur, called **black sulphur,** or **metallic sulphur,** was reported by

G. Magnus,[3] and F. Knapp. It is said to be formed when sulphur is repeatedly heated to about 300°, and abruptly cooled. G. Magnus called the product *roten oder schwarzen Schwefel.* He also obtained it by melting together equal parts of sodium carbonate and sulphur, since it is considered that liver of sulphur owes its coloration to this form of sulphur. The red, insoluble residue remaining when the liver of sulphur is treated with a soln. of potassium cyanide, washed and dried, is supposed to be black sulphur. When viewed in thin films by transmitted light, black sulphur appears intensely blue, and it imparts a blue colour to fused salts—borax, sodium and potassium chlorides, sodium sulphate, etc. E. Mitscherlich considered black sulphur to be ordinary sulphur coloured by admixed organic matter, and he showed that the presence of 0·002 part of fat is able to colour red a thin layer of sulphur, and a thick mass, black. G. Magnus, J. Moutier and M. Dietzenbacher, and A. Keller showed that numerous organic substances besides fat and metal sulphides will do the same thing when heated to 300°. H. C. Jones found that black sulphur remained as a residue when sulphur is burnt in air. G. Magnus and R. Weber, and F. Knapp regarded black sulphur as a special modification of the element. H. Biltz and G. Preuner showed that a black residue remains when sulphur is distilled, and R. von Hasslinger found that this residue is not the same as black sulphur since it contains an iron carbide formed by distilling sulphur with iron and a hydrocarbon, but not with iron alone. M. C. Schuyten assumed that *Schwefel sich bei langsamer Verbrennung an der Luft teilweise in Eisen verwandelt.* B. Neumann found black sulphur occurring native in Mexico, and concluded that the so-called black sulphur is not an allotropic modification, but ordinary yellow sulphur coloured black by small quantities of carbon or of metal—iron or platinum—sulphides. He said that the presence of carbon in the black sulphur is explicable on the assumption that the hydrocarbons in the volcanic exhalations from which the sulphur is deposited do not come into contact with sufficient air for complete combustion, with the result that carbon is deposited. The microphotographs of black sulphur show the presence of sulphur and amorphous carbon side by side. G. Magnus supposed that black sulphur is the cause of the dark colour assumed by viscid or plastic sulphur. W. Muthmann suggested that black sulphur is the metallic form corresponding with metallic tellurium and selenium (*q.v.*), and if so it should crystallize in the trigonal system.

According to F. Wöhler, R. Weber, F. C. and A. Vogel, and J. S. C. Schweigger, if a conc. soln. of ferric chloride be mixed with 50–100 times its vol. of a soln. of hydrogen sulphide, the liquid assumes a deep blue colour—**blue sulphur.** H. Schiff added that if a soln. of liver of sulphur be added to the ferric chloride soln., violet-coloured sulphur is formed, while if the ferric chloride soln. be added to the other soln. drop by drop, the colour passes from green to dark blue—*vide infra,* sulphur sesquioxide. J. W. Döbereiner noticed the blue colour of the colloidal soln. of sulphur obtained by oxidizing a soln. of hydrogen sulphide. A. Müller and H. Dubois obtained the blue colour when preparing carbon tetrachloride by the reaction: $CS_2+2S_2Cl_2=CCl_4+3S_2$ in the presence of ferric chloride; with aluminium chloride, the colour is darkened; and with cadmium chloride, green. C. J. Gil obtained a blue coloration when alcohol or acetone acts on ammonium, sodium, or calcium polysulphide. C. Geitner obtained an ephemeral blue colour on heating sulphurous acid and barium or strontium carbonate in a sealed tube at 120°–130°; by heating sulphur with water and hydrogen, metallic zinc, or aluminium hydroxide; and by heating an aq. soln. of hydrogen sulphide to 200° in a sealed tube—on cooling the blue colour disappeared. In general, the blue sulphur appears at the moment sulphur is formed; N. A. Orloff found that when a benzene soln. of sulphur monochloride acts on metal sulphides—especially bismuth trisulphide—a green, amorphous powder is formed which is not soluble in any solvent—water or acids—excepting carbon disulphide, to which it imparts a pale green tint. Uranyl sulphide, platinum disulphide, and silver sulphide give similar results with sulphur monochloride. Cadmium sulphide and sulphur monobromide boiled with toluene also yield blue or green sulphur; but with sulphur iodide, no such reaction occurs. Smaller yields are obtained if no solvent is used. Among the conditions of formation of this modification of sulphur, the most striking feature is the influence of dissociation on the incompleteness of the reactions by which it is formed. Such reactions are that of ammonium sulphide on alcohol or acetone. According to E. Paterno and A. Mazzucchelli, when 95 per cent. alcohol is mixed with traces of polysulphide there is produced a blue, and with larger quantities a green, coloration, but only when the alcohol is heated; in the cold, the liquid assumes a yellow colour. The reaction is sharper with potassium or sodium polysulphide than with the ammonium compound, but, in any case, the coloration is only transitory. With acetone the colorations are more intense and more persistent, the best results being obtained by adding an alcoholic soln. of potassium polysulphide to boiling acetone; even in the cold these solutions give a blue coloration, but this changes to green and ultimately to yellow with less quantities of the polysulphide than when boiling acetone is employed. The view that these colorations are due to a limited decomposition of the polysulphide is supported by the observations that intense and moderately persistent colorations are obtained with basic solvents such as pyridine, ethylamine, and allylamine, which are able to form saline compounds with persulphuric acid, whilst with water, the most highly dissociating solvent, no coloration is formed. It is also produced by the action of heat on potassium thiocyanate. Thus, according to E. Paterno and A. Mazzucchelli, when potassium thiocyanate is heated, it melts at 172·3° to a colourless liquid, which begins to turn blue at 430°, the colour gradually deepening to an intense indigo if this temperature is maintained. When the salt is cooled, the colour begins to fade at about 300°, but only disappears completely in the neighbourhood of the m.p. If the blue liquid is maintained at above 500°, it changes to an opaque, incandescent, red liquid, but again becomes blue immediately on cooling; even at this temp. there is no appreciable separation of free sulphur, although the thiocyanate retains a yellow colour after cooling. When heated in a current of oxygen at above 400°, potassium thiocyanate loses in weight rapidly, sulphate and polysulphide being formed. The reaction was also studied by W. B. Giles, and J. Milbauer. Green sulphur melts when heated and burns in air to an inappreciable residue; and it has all the properties of precipitated sulphur. The green powder loses its colour when dried or when acted on by water, alcohol, or ether, and it can be kept only under benzene, toluene, carbon disulphide, or olive oil. When placed under commercial xylene, it acquires first a blue and afterwards a red tint. When heated with persulphuric acid, the latter acquires a yellow colour; green sulphur is oxidized by hot nitric acid. P. P. von Weimarn found that a soln. of sulphur in glycerol or ethylene glycol is colourless, but when heated to 160°, it becomes clear blue, the depth of colour increases with rise of temp., and with the conc. of the sulphur. The colour is not due to an oxidation product in the solvent because it is not altered when oxygen is expelled by hydrogen or carbon dioxide. Acids—*e.g.*, boric acid—completely inhibit the colour, but the smallest addition of alkali suffices to intensify it to an indigo-blue. Methyl, ethyl, propyl, butyl, and amyl alcohols give either colourless or yellowish-green solutions of sulphur, but if a little alkali or alkaline-earth oxide be added, a blue or greenish-blue soln. is obtained. Similar results are given with acetone and even with water. Ammonium polysulphide soln. at certain dilutions, and sulphur dissolved in fused potassium thiocyanate or potassium chloride, show the same colour.

According to Wo. Ostwald and R. Auerbach, cryoscopic measurements with the clear blue solutions of sulphur in pyrosulphuric acid show the mols. to be diatomic. It is to be assumed that blue soln. in other solvents (*e.g.*, hot glycerol) also contain the sulphur in this form, which is thus much more highly dispersed than in most organic solvents in which the mols. are octatomic. There are two series of sulphur soln. of varying degrees of dispersion and varying colour. One is obtained, *e.g.*, by the progressive dilution of pyrosulphuric acid-sulphur soln. with water; and the second, *e.g.*, by the decomposition of thiosulphates with acid. The first series begins with the highly-dispersed S_2 mols. and passes through the colloidal range to coarse dispersions. The second begins at the smallest colloidal particles and finishes also at coarse suspensions. The colours of the first series start at pure ultramarine blue and pass to green, then to opalescent yellow, red, violet, then to a very turbid and impure blue and green, and finally to yellow, macroscopic sulphur. In the second series, the latter colours are more readily reproducible. They commence with the opalescent yellow and thereafter follow the same order. Sulphur soln. with sufficiently wide variations of dispersion thus pass through the visible spectrum twice, and thus furnish a colloidal analogue to the colours observed by J. Piccard with organic compounds. The colour changes are produced by the movement of three absorption bands. In molecularly dispersed (S_2) soln., two of these bands are in the ultra-violet, and one in the visible spectrum. With decreasing dispersity, the bands shift towards the longer wave-lengths. N. A. Orloff infers that a blue modification of sulphur really exists, that it appears green when mixed with yellow sulphur, and that it is very unstable, being able to exist at the moment of its formation in certain reactions, and in a peculiar state of fixation in some inorganic or organic compounds. Thus, bismuth, zinc, or cadmium sulphide furnishes a green sulphur which dries white, and which is associated with a little of the metal chloride. H. Moissan observed coloured soln. were obtained with sulphur and liquid ammonia (*q.v.*), and likewise also A. Stock and M. Blix. J. Hofmann suggested that the blue colour of a soln. of disulphur trioxide in conc. sulphuric acid, observed by C. F. Bucholz, is due to the presence of a trace of colloidal sulphur. Wo. Ostwald obtained coloured soln. of sulphur by putting pieces of ordinary sulphur in boiling glycerol. R. E. Liesegang obtained a blue soln. by the action of citric acid on a gelatinous soln. of sodium thiosulphate. If the reaction goes too slowly, the colour disappears. The phenomenon is attributed to the high degree of dispersion of the precipitated sulphur. Coloured soln. of sulphur in boric oxide, phosphorus pentoxide, potassium thiocyanate, potassium cyanide, and glycerol were observed by J. Hofmann; and in ethyl alcohol and acetone, by E. Paterno and A. Mazzucchelli. C. Geitner also referred to the colour of some minerals—celestine, heavy spar, flint, hauyne, etc.—supposed to be due to the blue modification of sulphur. C. Geitner, and G. N. Lewis and co-workers observed that when sulphur is heated in quartz with dil. neutral or slightly alkaline soln. of non-reacting salts such as potassium chloride, sodium sulphate, magnesium sulphate or potassium orthophosphate, a blue colour of the shade of indigo appears, and is first noticeable, in a tube of 0·5 cm. diameter, at about 130°. The intensity of the colour increases rapidly with the temp. On cooling, the colour disappears and milky sulphur is precipitated. Pure water in quartz gives no colour with sulphur, but in glass the colour appears, owing doubtless to the dissolved alkali. In the presence of acid this colour does not appear. A. Colson, and J. B. Senderens made some observations on this subject. N. A. Orloff likens the formation of blue sulphur by oxidizing hydrogen sulphide with ferric chloride soln. to the formation of ozone by oxidizing water with fluorine; it was suggested, solely by the analogy with this reaction, that, like ozone, O_3, the mol. formula is S_3, and this hypothetical compound has been called **thiozone**. The analogy is a poor one. The argument has been supported by the observation that sulphur in certain combinations produces an intense coloration as in the **thiozonides** of H. Erdmann. E. Paterno and A. Mazzucchelli added that the properties of blue sulphur and ozone allow of no such analogy being drawn. They also found that when sulphur is vaporized in a transparent, quartz vessel, it is seen that it has at first a deep, reddish-yellow colour, which, at higher temp., becomes very faint, and is ultimately replaced by a characteristic, pale-blue colour, this disappearing when the vapour cools. The same blue colour is observed when sulphur is volatilized in an atmosphere of carbon dioxide, but not when an atmosphere of sulphur dioxide is employed. N. A. Orloff, and F. Knapp regard the blue colour of ultramarine (*q.v.*) as due to the presence of sulphur in a special state of aggregation, a view not held by some workers because the blue colour is retained at a red-heat. This subject was also discussed by J. Hofmann.

O. C. M. Davis and F. W. Rixon associate the chromogenetic properties of sulphur with the energy of combination, and more particularly with the energy left unabsorbed from the gross energy of the system, though in the case of sulphur itself, the variations in colour may be due to the sizes of the particles, and variations in intermolecular structure. The colour of ordinary sulphur and of plastic sulphur, and of the polysulphides; the yellow sulphur mono- and di-chlorides; the brownish-red sulphur tetrachloride; the yellowish or greenish-yellow soln. of sulphur dioxide in conc. soln. of alkali or ammonium hydrosulphites; the yellow compounds of thiosulphates and sulphur dioxide; and the yellow compounds of sulphur dioxide with potassium iodide or thiosulphate are of interest. In the colourless sulphur compounds—sulphides, hydrosulphides, hydrogen sulphide, sulphites, sulphates, thiosulphates, and polythionates—H. Bassett and R. G. Durrant have pointed out that the sulphur atom is surrounded by a shell of 8 electrons, and the co-ordination number ranges from zero in the case of the S''-ions to 4 in the case of the sulphates. Hence the lack of colour is assumed to depend on the presence of an outer shell of 8 electrons, and to be independent of the co-ordination number of the atom. The sulphur atom in colourless sulphur hexafluoride has an outer shell of 12 electrons. They assume that *an outer shell of* 10 *electrons determines the visible colour produced by sulphur*, although the actual colour of a particular compound must depend on its structure and composition as a whole. Thus, the union of a 10-electron sulphur atom with one of 8 electrons may promote the colour in a similar way to that assumed by R. Willstätter and J. Piccard in organic compounds with a meriquinonoidal structure. This is the case with yellow sulphur tetrachloride; in potassium thiocyanate when associated with sulphur dioxide; in the greenish-yellow sulphite soln. containing $H_2SO_3.SO_2$; and in the yellow thiosulphate soln. associated with sulphur dioxide and containing $K_2S_2O_3.SO_2$. Potassium chloride and bromide form colourless compounds with sulphur dioxide, so that the coloured compound with potassium iodide must be connected with the iodine. Sulphur dichloride on this hypothesis should be colourless; its yellow colour may be dependent on association in the liquid state—that is, the co-ordination of a molecule with the sulphur atoms of other molecules. The colour of sulphur and the polysulphides is based on a colourless  $\mathrm{S}<\begin{matrix}\mathrm{S}\\ \vdots\\ \mathrm{S}\end{matrix}$ molecule in which all the sulphur atoms have 8-electron outer shells, or of a S : S.S-molecule in which each sulphur atom has an 8-electron sheath. Hydrogen disulphide, H.S.S.H, is colourless, but in yellow hydrogen trisulphide, one of the sulphur atoms has a 10-electron sheath. It is not probable that the sulphur–sulphur linkages in themselves have any great influence on the colour because thiosulphates and polythionates have these linkages and are yet colourless. M. Delépine showed that, as a rule, compounds containing sulphur singly linked to carbon are not coloured, while those having sulphur doubly linked to carbon are coloured if the molecule also contains an acid group acting as an auxochrome—*e.g.*, the dithiocarbamates of J. von Braun and F. Stechele. J. E. Purvis and co-workers showed that the bivalent S : C-group must be regarded as a powerful chromophore—*vide infra*, absorption spectra. H. Lecher attributed the darkening of the yellow colour of diphenyl disulphide, $(C_6H_5)S.S(C_6H_5)$, which occurs when this compound is heated, not to a dissociation into free radicles, or to a rearrangement of the atoms, but to a redistribution of the valencies.

P. P. von Weimarn showed that sulphur dissolves with an indigo or blue coloration in water, ethyl, propyl, *iso*butyl, and amyl alcohols, acetone, glycerol, and ethylene glycol if these solvents are rendered alkaline; with the last two solvents it is, indeed, unnecessary to add alkali, but this may come from the glass. When these solvents are neutral or acidified, no blue colour appears. Any soln. of a polysulphide becomes blue when heated if the solvent is not acid in character, and does not decompose sulphides in general, and by variation of the conc. and temp. such soln. may be obtained of any colour in the spectrum. The blue colour observed in the above cases and that exhibited by fused potassium chloride and sulphur, soln. of sulphur in ammonia or sulphur trioxide, etc., occurs when the linking of the sulphur in these compounds, which are classed together as "sulphydrates," is weakened, that is, when the sulphur atoms approach a condition of freedom from combination. The blue colour may appear over an interval of temp. ranging from $-80°$ to $+800°$. W. Biltz referred colour to unsaturation. The subject was also discussed by W. Kossel, J. Meisenheimer, and Wo. Ostwald and R. Auerbach—

vide infra, sulphur sesquioxide. P. P. von Weimarn inferred from the widely different nature of the solvents which form blue soln. of sulphur, and the necessity of their being alkaline or neutral, that the colour is due to the formation of polysulphides in which the sulphur is held by a specially weak linking. The presence of single sulphur atoms or of combinations of sulphur atoms, not stable under ordinary conditions, is regarded as possible. The blue colour of sulphur sesquioxide (soln. of sulphur in sulphur trioxide) and of compounds of nitrogen and sulphur (soln. of sulphur in liquid ammonia) is held to be due to the same condition of the sulphur atoms. All such compounds are embraced by the term *sulphurates*, and they give true soln. A classification of blue sulphur soln. is made in which, in addition to the sulphurate group already described, three other groups are defined as follows: (i) in which the colour is observed only by reflected light, *i.e.* due to opalescence; (ii) in which the colour is observed by transmitted light, but is due to the scattering of light from comparatively coarse colloid particles; and (iii) in which the colour depends on the relation between the refraction coeff. of the dispersing and dispersed phases—*vide infra*, sulphur sesquioxide.

According to R. Auerbach,[4] **colloidal sulphur** is capable of exhibiting various colours dependent on its degree of dispersion, or the fineness of its particles. The colour changes are well shown by adding a soln. of 0·1 c.c. of phosphoric acid of sp. gr. 1·70 in 9·9 c.c. of water to a 0·05*N*-soln. of sodium thiosulphate. There is first a feeble turbidity, then a yellowish-blue opalescence, and this is followed successively by yellow, green, red, violet, and blue colorations, and finally in about 20 minutes, sulphur is precipitated. As previously indicated, C. L. Berthollet in 1798, J. Dalton in 1808, and J. W. Döbereiner in 1813, prepared a **colloidal solution of sulphur** by the action of sulphur dioxide on an aq. soln. of hydrogen sulphide; and H. W. F. Wackenroder observed that "if the liquid be frozen and thawed, a great part but not all the suspended sulphur separates out; and if a neutral salt of an alkali, like sodium chloride, be added to the acidic liquid, all the sulphur is immediately precipitated in large flocks." Four years later, A. Sobrero and F. Selmi investigated the sol, and concluded:

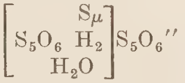
> If water is added to it, it divides up, forming an emulsion, from which it does not separate out, even on prolonged standing (several months). . . . If a little aqueous soln. of a neutral potassium or sodium salt is added to the emulsion, sulphur is immediately precipitated, but, singularly, if a sodium salt is used, the sulphur does not lose the property of dividing itself up again in water. All that is necessary is to decant the liquid containing the sodium salt, and to wash the precipitate several times with distilled water; after the second or third washing the sulphur does not settle out, but regenerates the emulsion. If a potassium salt, especially the sulphate, has been used, the precipitated sulphur has completely lost the property of emulsifying in water. . . . In spite of repeated washing, it always retains a trace of the potassium sulphate employed for the precipitation. . . . This enormous quantity of sulphur is, one would be inclined to say, dissolved, for it hardly affects the limpidity of the liquid. . . . Sulphur can thus be modified in an extraordinary manner by the substances present at the time of deposition, these adhering obstinately, probably by simple adhesion, and can either acquire the property of emulsifying in water, or assume a state of aggregation which prevents it dividing up in water. It thus appears that sulphur exhibits phenomena analogous to those observed with many other substances, which possess the power of dispersing and dividing themselves in a liquid, without completely dissolving in it, as *e.g.* soap, starch, and prussian blue, on which F. Selmi has previously made observations similar to those now described. These facts are related to a set of phenomena which F. Selmi has classed together under the name of pseudo-solutions. The number of pseudo-soluble substances seems to be rather large.

H. Debus obtained the colloidal sulphur, which he called *δ-sulphur*, by passing hydrogen sulphide into sulphurous acid. The term δ-sulphur is here employed for a variety of crystalline sulphur. R. Engel obtained it by the action of hydrochloric acid on thiosulphuric acid—C. A. L. de Bruyn used about 0·5*N*-HCl and 0·5*N*-$Na_2S_2O_5$, and W. Biltz and W. Gahl also found that a colloidal soln. of sulphur is produced by the hydrolysis of thiosulphuric acid (*q.v.*). M. Raffo found that in order to separate the soluble and insoluble sulphur, the thick, cloudy liquid is diluted somewhat, heated to 80°, and filtered through glass-wool. It is then left in a cool place for 12 hours, again heated and filtered, and these operations are repeated until the whole of the insoluble sulphur has been removed. The end-product is a cloudy, yellowish-white mass, which, on warming, yields a perfectly clear, yellow liquid. On cooling, the colloidal sulphur separates, and is removed by centrifuging, washed with a little cold water, again centrifuged, and dissolved in the least possible quantity of water. The liquid is neutralized by addition of sodium carbonate, which causes the sulphur to separate, and, after centrifuging, a residue of very nearly pure soluble sulphur is obtained. On removing the sodium sulphate from the neutralized soln. by dialysis, the soln. becomes unstable and insoluble sulphur separates. Hence, a pure aq. soln. of colloidal sulphur cannot be obtained. Coagulation also occurs on the addition of various electrolytes. The sulphur precipitated by sodium chloride or nitrate dissolves on warming or on dilution, and that precipitated by potassium chloride, nitrate, or sulphate is insoluble. Precipitation does not take place, in general, on the addition of ammonium sulphate, nitrate, or chloride, or of sodium sulphate. Dilute un-neutralized soln. remain clear for long periods, although small quantities of rhombic and monoclinic sulphur are gradually deposited. Conc. soln. become cloudy in consequence of the separation of insoluble sulphur. M. Raffo and J. Mancini concluded that definite amounts of electrolytes are necessary for a stable sol. Potassium salts are more active than the corresponding sodium salts; whilst these are a little less effective than magnesium or zinc salts. M. Raffo and G. Rossi showed that if the sulphur in a colloidal soln. is precipitated by sunlight, the electrical conductivity of the resulting aq. soln. containing sodium sulphate and sulphuric acid is very much larger than that of the original colloidal soln. When further quantities of the sulphates are added to the colloidal sulphur soln., the observed increase in conductivity agrees, however, with that calculated on the assumption that the sulphur is without influence on the added electrolytes. These facts seem to show that the sulphates originally present in the colloidal soln. are in some way associated with the sulphur. This condition cannot be attained by the subsequent addition of the salts to the colloid. H. Vogel, and H. Bovel modified the process. M. Schaffner and W. Helbig treated hydrogen sulphide with sulphur dioxide in a soln. of calcium or magnesium chloride; I. Guareschi passed a mixture of hydrogen sulphide and sulphur dioxide through water, and found that the latter becomes milky owing to the deposition of colloidal sulphur, which is precipitated in arborescent formation and falls from the surface to the bottom of the liquid in spirals, each of which is terminated by a ring similar to the vortex-rings. E. Dittler observed that when steam acts for a prolonged period on pyrites or marcasite, small quantities of colloidal sulphur are produced. R. H. Brownlee found that the amorphous sulphur, from sulphurous acid and hydrogen sulphur, contains 79 to 82·6 per cent. of insoluble sulphur. C. J. Fritzsche, and C. Brame mentioned the utricular form of the particles of colloidal sulphur. J. Stingl and T. Morawsky said that at the moment of separation the particles of sulphur have a spherical form; and in the presence of salt soln., the spherules flocculate together. The action of the salts does not follow stoichiometrical laws, but the effect is physical. The Chemische Fabrik von Heyden prepared colloidal sulphur, for medicinal purposes, by precipitating sulphur from its soln. in the presence of protective colloids, say an albumenoid, redissolving the product in a dil. soln. of alkali hydroxide, and precipitating by alcohol, a mixture of alcohol and ether, or acetone. A. Himmelbauer prepared colloidal sulphur by the action of gelatine or colloidal silica on a soln. of hydrogen sulphide; L. Sarason, by acidulating soln. of thiosulphates in glycerol thickened with gelatine; and by decomposing soln. of sulphur dioxide and hydrogen sulphide in volatile solvents—carbon disulphide or tetrachloride, benzene, etc. According to H. Vogel, the two gases are passed simultaneously into water containing a protective colloid. The hydrogen sulphide is kept in excess, in order to increase the yield of colloidal sulphur and to reduce the formation of polythionic acids. The size of the particles depends on the temp. of the liquid, and is less than $25\mu\mu$ when the temp. is kept between $-3°$ and $4°$. For storage, the soln. are placed in closed receptacles while still saturated with hydrogen sulphide. The Aktiebolaget passed a mixture of these two gases into 0·1*N*-acid, and precipitated the colloidal sulphur with sodium chloride. The gel may be converted into a sol in the usual way. J. Meyer saturated a few c.c. of a soln. of hydrazine sulphate with ground sulphur, and poured a few drops of the soln. into several litres of water, with vigorous agitation. P. P. von Weimarn and co-workers based a process for preparing colloidal soln. of sulphur on the rapid condensation of the mols. of the dissolved substances when the solvent, alcohol, is replaced by a dispersion medium, water, which dissolves the solvent, but dissolves very little or none of the sulphur. If a conc. soln. is added to such a dispersion medium, fine disperse particles are obtained, but not colloidal soln. E. Müller and R. Nowakowsky prepared colloidal soln. of sulphur by the cathodic disintegration of a piece of sulphur fused on the platinum with an e.m.f. of 220 volts. T. Svedberg also obtained the colloidal sol by an electric discharge; and H. H. Wilkinson, by condensing the vapour in vacuo. F. Sekera sprayed a soln. of sulphur in a solvent into a room hot enough to evaporate the solvent. Wo. Ostwald and I. Egger obtained the colloid by pouring a soln. of sulphur in hydrazine hydrate into hot water, and dialyzing the product.

The Thomsen Chemical Co. prepared colloidal sulphur by grinding it with a colloid—say, 50 parts of sulphur, 5 of glue, and 50 of water; other protective colloids can be used—extract of soap-bark, Irish moss, gum tragacanth, or gum arabic. The soln. is not precipitated by sulphuric acid, and is used as an insecticide. P. Ducancel and H. Gouthière incorporated very finely-divided sulphur with a saccharate of an alkaline earth, and found that the product is miscible with water. It is used for the treatment of vine diseases. W. F. Sutherst and H. Philipp, and F. C. Elphick and J. R. Gray prepared colloidal soln. of sulphur from the polysulphides. A. Mittasch and F. Winkler, and the Hevea Corporation mixed resin, soap, or other protective colloid with an aq. soln. of a polysulphide and then treated the mixture with an acid; and J. Y. Johnson used soap, gelatin, cæsein, sulphite cellulose waste liquor, glycerol, etc., as protective colloid. M. Lora and M. Tamayo obtained a hydrosol by adding drop by drop with stirring a hot alcoholic soln. of sulphur to an equal vol. of a one per cent. soln. of gelatin, and heating the mixture under reduced press. until half the alcohol had evaporated. A. Gutbier passed superheated sulphur vapour free from air into air-free water, and obtained a white sulphur hydrosol containing up to 0·082 per cent. S. The soln. has an acidic reaction owing to the presence of traces of polythionic acid and water. Sols with a higher sulphur content—up to 0·85 per cent.—were made by condensing sulphur vapour in dil. soln. of organic protective colloids—*e.g.* 0·5 per cent. saponin or a 1·0 per cent. soln. of starch. H. Plauson, A. J. Auspitzer, P. P. von Weimarn and S. Utzino studied the colloidal sulphur soln. obtained by grinding sulphur with dextrose, etc. S. Roginsky and A. Schalnikoff obtained the colloid by condensing the vapour on a surface cooled by liquid air.

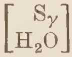
According to R. E. Liesegang, if a few drops of a 20 per cent. soln. of citric acid be placed on a thin layer of a solidified soln. containing gelatin and sodium thiosulphate, the precipitation of sulphur which results from the diffusion of the acid is accompanied by the development of colour effects. In transmitted light, the colour is a deep lilac-blue. The colour is not due to interference, but appears to be determined by the size of the colloidal particles. After about twenty-four hours, the colour effects disappear, and this is supposed to be due to the conversion of S_μ into S_γ. A. Lottermoser examined the particles with the ultramicroscope. R. Zsigmondy measured the osmotic pressure. S. Odén showed that in the coagulation of colloidal soln. of sulphur of different degrees of dispersion, the conc. of electrolyte necessary for coagulation increases as the suspended phase becomes more highly dispersed. The stability of the sol towards sodium chloride and hydrochloric acid increases with the dispersion of the sol; but S. Utzino found that the maximum stability does not occur with colloidal soln. with particles in the finest state of subdivision. S. Odén prepared sulphur hydrosols with particles of nearly uniform sizes. In T. Svedberg's relation between the solubility, C, of colloidal sulphur, the temp., θ, and the conc. of the dissolved electrolyte, $C=e^{k(\theta-\theta_0)}$, where C denotes the percentage conc. of the colloidal sulphur; and θ_0 and k are constants depending on the degree of dispersion of the hydrosol, and the conc. of the electrolytes in soln., it was found that for a given dispersion, k is nearly independent of the conc. of the electrolyte—sodium chloride—whilst θ_0 increases with the quantity of the coagulant. For a given conc. of the salt, k and θ_0 diminish as the degree of dispersion of the hydrosol increases, the rate of diminution of θ_0 being much greater than that of k. The addition of acids in small quantities reduces the value of θ_0, while k remains unchanged. If the particles are of different sizes, the equation no longer represents the relation between the coagulum and the soln. on the temp. S. Odén studied the sp. gr., the viscosity, and the surface tension of colloidal soln. of sulphur; D. N. Chakravarti and N. R. Dhar, the viscosity; and P. P. von Weimarn and S. Utzino found the life-curves of dispersed sulphur supported the theory that adsorption and chemical forces are essentially the same. G. Quinck found that the particles have a negative charge and travel cataphoretically to the anode during the electrolysis of a colloidal soln. of sulphur. I. Parankiewicz calculated the elementary charge on the particles to be of the order 10^{-13} electrostatic units; R. Bär gave 10^{-10}; and K. Wolter, $4{\cdot}8\times10^{-10}$. A. F. Guerasimoff studied the electrical endosmose of sulphur sols. D. N. Chakravarti and N. R. Dhar found that the sp. electrical conductivity of a sol of sulphur with 3·5 grms. of sulphur per litre changed from $3{\cdot}84\times10^{-3}$ to $3{\cdot}06\times10^{-3}$ in 89 days, and the viscosity changed from 0·00989 to 0·01054.

P. Bary said that colloidal sulphur in the form of a limpid liquid is a hydrophilic colloid, capable of absorbing water. This absorption is favoured by the presence in soln. of small amounts of salts of univalent metals, whilst it is prevented by the action of salts of bivalent metals. Such colloidal sulphur is not pure sulphur, but a compound containing sulphur in a highly polymerized state. The compounds are easily dissociable, and only exist in aq. medium in the presence of substances which limit their decomposition. When the swelling of the granules, due to the absorption of water, becomes small, the granules lose their transparency and the liquid becomes milky and loses its stability. According to H. Freundlich and P. Scholz, colloidal sulphur obtained by the interaction of hydrogen sulphide and sulphur dioxide, or by the decomposition of the thionic acids, are hydrophilic, whilst that obtained by pouring an alcoholic soln. of sulphur into water is hydrophobic. Hydrophobic sulphur is negatively charged, and it is coagulated by electrolytes according to the general laws concerning the coagulation of hydrophobic sols, namely, (i) the strong influence of the adsorbability and valency of the cations, (ii) the strong effect of the hydrogen-ion, and (iii) the slight effect of the hydroxyl-ion. The sols may only be prepared in relatively small concentrations, the coagulum is not peptized by washing with water, and the sols may be preserved for a day or two only. The coagulation of the hydrophilic soln. is markedly different; and the difference is shown mainly in the following points: (i) alkali salts have a ten to twenty times weaker coagulating action than with Weimarn's sol; (ii) the lyotropic series of the cations is well-defined; lithium-ions have a very weak coagulating action, whilst sodium-, potassium-, rubidium-, and cæsium-ions are markedly and increasingly stronger; (iii) acids have a still weaker coagulating action than the alkali salts; (iv) alkalies convert the hydrophilic sol into one with properties similar to those of the hydrophobic sol. The assumption that the micellæ of the hydrophobic sol consists of λ-sulphur and those of the hydrophilic sol of μ-sulphur is not sufficient to explain the differences, because the behaviour towards either bases is not explained. A possible explanation is that the hydrophilic sol contains pentathionic acid, while the hydrophobic sol does not. The presence of pentathionic acid is proved by (i) the acid can be detected in the filtrate from coagulated sulphur by the fact that on the addition of alkali more sulphur is deposited; (ii) prolonged action of alkali on coagulated sulphur or sulphur micellæ brings about the formation of thiosulphate ; this action is brought about by ammonia without the sulphur itself being markedly attacked. It is probable that the pentathionic acid is adsorbed in the sulphur particles, since this substance is very difficult to remove by washing. The quantity of pentathionic acid bound to the sulphur is found to be 0·1 to 0·7 millimol. per gram of sulphur. The influence of pentathionic acid on the stability of the hydrophilic sol is explained by assuming that this acid has a constitution closely related to that of water and sulphur, and therefore facilitates the formation of micellæ, which, in addition to sulphur and pentathionic acid, contain large quantities of water. The greater water content of the hydrophilic sol is indicated by its greater transparency when compared with a hydrophobic sol of equal sulphur content. The micellæ are represented by



$$\left[\begin{array}{c} \quad S\mu \\ S_5O_6\ H_2 \\ H_2O \end{array}\right]S_5O_6''$$

Hydrophilic sol.



$$\left[\begin{array}{c} S\gamma \\ H_2O \end{array}\right]$$

Hydrophobic sol.

This hypothesis explains the behaviour on coagulation when (i) alkalies decompose the pentathionic acid, whereby the loose combination between the sulphur and water is also disturbed and converted into one which is similar to that of the hydrophobic sol ; and (ii) acids have such a feeble coagulating power because they increase the stability of the pentathionic acid and produce more pentathionic acid from the pentathionates which may be present. The structure also is in keeping with the fact that hydrogen sulphide has an action on the sol similar to that of the alkalies ; that is, it converts it into a hydrophobic sol which is much less stable because the pentathionic acid is decomposed by hydrogen sulphide with separation of sulphur. Further, sols of the same nature as hydrophilic sol are obtained by reactions which produce both sulphur and pentathionic acid ; for example, the decomposition of sulphur monochloride by water : $5S_2Cl_2+6H_2O=5S+H_2S_5O_6+10HCl$. The stability of hydrophilic sol, which is due to pentathionic acid, does not depend on the charge of the micellæ. Whether or no hydrophilic sol contains $S\mu$ cannot be definitely answered, although the yellow colour of the sol makes it extremely likely that this variety of sulphur is present. The peptization and coagulation of sulphur hydrosols was studied by A. Gutbier, P. C. L. Thorne and co-workers, A. Fodor and R. Rivlin, A. von Buzagh, G. Rossi, Wo. Ostwald, N. N. Andreeff, A. Ivanitzkaja and L. Orlova, S. Odén, S. Ghosh and N. R. Dhar, A. von Buzagh, H. B. Weiser and G. E. Cunningham, W. A. Dortman, E. Iwase, H. Freundlich, and G. Rossi and A. Marescotti. I. D. Garard and F. M. Colt found that soln. of sulphur in benzene, toluene, xylene, kerosene, acetone, and ethyl acetate were prepared by the reaction between hydrogen sulphide and sulphur dioxide. The benzene sols had a deep yellow colour and contained 1·4 to 1·8 per cent. of sulphur. At the end of four months, one sample gave no indication of coagulation ; it was affected little or not at all by the electrolytes and organic substances which were tried as coagulants. When the benzene was removed by evaporation, there remained a sticky, yellow residue of amorphous sulphur, which could not be re-dispersed in benzene. It dialyzed more slowly than dissolved sulphur through membranes of ox-bladder and of cellulose acetate. It seems doubtful whether either water or acids is responsible for the stability of these sols. E. Iwase studied the action of mercaptan on the life-period of the sol. L. S. Bhatta and co-workers observed that the addition of gelatin first makes the colloid more sensitive to coagulation by potassium chloride, and with more gelatin, the soln. becomes stable.

F. L. Browne ascribed variations in the heat of coagulation of a sulphur hydrosol with the coagulant and with conc., to the heats of mixing of the coagulants with the polythionic acids in the sols, as well as to incidental changes in adsorption. Sulphur in the coagulum is in the same allotropic state as in the sol. G. Rossi examined the coagulation of colloidal sulphur soln. by electrolytes. The amount of potassium chloride or bromide required for flocculation increases with the proportions of sulphuric acid and sodium sulphate present in the soln. The quantity of potassium permanganate adsorbed by sulphur is greater with dialyzed than with non-dialyzed sulphur. J. Traube and E. Rackwitz discussed the action of protective colloids. M. Raffo and G. Rossi showed that with a series of salts of the same metal, the precipitation increases with the formula weight of the anion—but nitrates are exceptional. The amount of sulphur precipitated by a fixed quantity of the same electrolyte decreases as the conc. of the sodium sulphate and sulphuric acid increases. The sulphuric acid and sodium sulphate are regarded as crystalloids of formation. The electrical conductivity of a soln. of colloidal sulphur containing sulphuric acid and sodium sulphate is lower than that of a similar soln. containing no colloidal sulphur. The b.p. of a soln. of the same kind as the above is lower after the colloidal sulphur has been removed than when the colloid is present. Further, if a colloidal sulphur soln. containing sulphuric acid and sodium sulphate is dialyzed to remove the electrolytes, and the same amount of electrolytes added to the dialyzed soln., then the electrical conductivity has the same higher value of the soln. from which the colloid has been removed. Hence, the action of the colloidal sulphur extends to sulphuric acid and sodium sulphate even when these are present in quantities larger than those required to stabilize the sol, provided that the excess of these substances was present when the colloid was formed. Additional quantities of these substances added after the formation of the colloid are not affected by the colloid. It is therefore assumed that crystalloids, in the form of sulphuric acid and sodium sulphate, undergo a change in their physical nature in the presence of colloids, which is shown by a reduction in the electrical conductivity and the osmotic press. H. Rinde studied the adsorption of ions of colloidal sulphur. H. Freundlich and E. Schalek measured the viscosity of colloidal soln. of sulphur; I. Lifschitz and J. Brandt, the refractive index of colloidal soln., and found the μ-formula gave more constant results than the μ^2-formula; N. Pihlblad measured the adsorption of light by soln. with particles of different sizes. Colloidal soln. containing particles for which the average diameter is $550\mu\mu$, give a flat absorption curve without any evidence of a maximum. For particles of average diameter $=160\mu\mu$, the absorption is greater, and a maximum occurs at $\lambda=340\mu\mu$; for particles of diameter$=110\mu\mu$, the maximum shifts to $\lambda=280\mu\mu$; and for more highly dispersed soln., no maximum was found within the limits of observation, but with diminishing size of the particles, the curve of absorption approximates continuously to that of a molecular soln. G. I. Pokrowsky studied the dispersion and polarization of light by sulphur suspensions; and Y. Björnstähl, the birefringence. G. I. Pokrowsky found that the dispersion of the particles produced by the decomposition of thiosulphuric acid is in agreement with Lord Rayleigh's theory of dispersion. P. Lal and P. B. Ganguly studied the action of ultra-violet light on the colloid.

When sulphur is heated, it melts at about 115° to form a brownish-yellow, transparent, mobile liquid; as the temp. rises, the liquid becomes more and more viscid and at the same time it becomes dark reddish-brown, and is no longer transparent except in thin films. Between 220° and 250°, the sulphur is so viscid that it does not run out when the containing vessel is inverted. At a still higher temp., the sulphur again becomes more fluid, but not so much as it was at 120°. It also acquires a greater transparency, but remains brown. If this liquid, or if the viscid liquid be suddenly quenched by pouring it into cold water, a soft, elastic product is obtained—*plastic sulphur*—which hardens in the course of a few days. T. Iredale[5] prepared *elastic sulphur* by treating powdered sodium thiosulphate with one-half its weight of conc. nitric acid, and after the reaction is complete, adding water and washing the product. A yellow, elastic, transparent mass is obtained which after distension to four times its length will regain its original form. Cooling to 0° makes it opaque and brittle, but heating in water to 100° reproduces the elastic characteristics. After 24 hrs., it passes completely into the crystalline form. P. P. von Weimarn found that when sulphur at above 400° is poured in a thin stream into liquid air, it is obtained in the form of a thin thread of diameter 0·5–1 mm. When removed from the liquid air, this thread is quite hard and brittle, but, when the temp. rises somewhat, it assumes extraordinary elasticity. This sulphur has a polished surface, and appears pale grey in reflected light and pale yellow in transmitted light, being completely transparent and without sign of opalescence. The maximum extension of a thread about 1 mm. in diameter is approximately 5·5 times the original length, and if the extension is less than the maximum, the thread is able to return almost to its original length. The elasticity is lost in about half an hour after the thread is removed from the liquid air, the sulphur then becoming plastic and remaining so for about twenty-four hours. According to J. Dussy, when liquid sulphur, tempered between 157° and 175°, solidifies very rapidly, it has a characteristic vitreous appearance. Sulphur heated to 220°, poured suddenly into cold water, and allowed to cool in contact with it, yields an outer layer of plastic sulphur, an intermediate layer of *vitreous sulphur*, and an inner core of the prismatic variety. This vitreous form seems to be the analogue of the well-known vitreous selenium. A. Wigand regarded plastic sulphur as a liquid with a very great internal friction. G. Magnus, and C. J. St. C. Deville regarded plastic sulphur as a soluble variety of amorphous sulphur. M. L. Frankenheim explained the change in the viscosity of molten sulphur by assuming that at 260°, where a break occurs in the heating curve, a new liquid state of sulphur appears. The new liquid variety of sulphur is formed at 170°, and an increasing proportion is produced as the temp. rises. He said that between 170° and 260°, the mass is an emulsion of minute droplets of two liquids, and owes its viscosity to the ascendency of the surface properties over those natural to either liquid taken separately. But, according to the phase rule, one substance cannot exist in 3 phases—two liquid and one vapour—except as non-variant system which cannot have an extended region of stability. J. H. Kastle and W. P. Kelley said that plastic sulphur is composed of several molecularly different kinds of sulphur, all of which are amorphous. G. Quincke assumed that there are four forms of sulphur which are stable respectively between the limits 0°–96°, 96°–160°, 160°–300°, and 300°–448°; further, that liquid sulphur has a jelly-like cellular structure, and represents a mixture of solutions containing these allotropic modifications in different proportions, the several solutions being separated by limiting surfaces in which surface-tension forces play an important part. At one and the same temp., liquid sulphur may contain soln. in which these modifications are present in different proportions, this being determined by the previous physical treatment of the sulphur.

C. M. Marx observed irregularities on the heating and cooling curves of sulphur; and M. L. Frankenheim showed that different specimens gave different results which he attributed to irregularities due to unequal heating or cooling owing to changes in the viscosity. All specimens agreed, however, in giving marked absorption of heat on the heating curve at 250°–260°, and on cooling, an evolution of heat. C. J. St. C. Deville, on the contrary, found the behaviour at 250°–260° quite normal, but he observed on the heating curve an evolution of heat at 120°–160°, and also at 180°–230°; while the cooling curve gave a slight evolution of heat at 240°–210°; an absorption at 180°–160°; a slight evolution at 160°–145°; and an absorption at 145°–135°. He considered the evolution of heat between 240° and 210° to be the only significant part of the phenomena, and this he attributed to the great viscosity of sulphur between these temp. K. Schaum observed a notable absorption of heat near 168°. A. Smith and W. B. Holmes showed that the effect is so sensitive to the effects of various degrees of superheating, and undercooling, that even when the sulphur is constantly agitated, the results are of no value in establishing the existence of transition points.

As indicated above, when molten sulphur is cooled, rhombic crystals of α-sulphur separate if the temp. is below the transition point, and monoclinic crystals of β-sulphur separate above that temp. This subject has been discussed by C. Brame, P. Schützenberger, J. Fritzsche, etc. D. Gernez showed that if the undercooled liquid be seeded with rhombic sulphur, the rhombic crystals will form and separate; similarly also with monoclinic sulphur. R. Brauns observed that during the freezing of molten sulphur monoclinic and rhombic crystals, aggregates of radial threads, and trichitic aggregates—*i.e.* bunches of hair-like crystallites—may be formed. P. Gaubert said that if sulphur be heated above 160°, and then suddenly cooled, a modification is produced which is slightly birefringent, and is blue by transmitted light. The blue colour is due to the fibrosity of the spherolites. Amongst these spherolites are some formed by very slender fibres having a spiral winding. They exhibit numerous varieties, but it is possible to obtain perfect spherolites the crystalline particles of which are wound round the mean index. The fibres rarely show more than three turns in the winding, the distance between the coils varying from one spherolite to another, and generally not exceeding 0·2 mm. Some amorphous sulphur, insoluble in carbon disulphide, is formed if the molten sulphur is heated above its m.p. According to B. C. Brodie, the formation begins above 120°; C. J. St. C. Deville said at 150°; and M. Berthelot, at 155°. In order to obtain a maximum formation of the insoluble sulphur, the molten sulphur should be heated until the viscid mass has become a mobile liquid, and then rapidly cooled, and the sulphur should be kept in a molten state for a long time—J. B. A. Dumas said at 230°–260°; C. J. St. C. Deville, at 260°; A. Schrötter, at 360°; and B. C. Brodie, at the b.p. The formation of the insoluble sulphur, said C. J. St. C. Deville, proceeds slowly at 155°, but is rapid at 170°; and no more is formed by heating at a higher temp. Quenching the molten sulphur in cold water furnishes about 35 per cent. of insoluble form; G. Magnus and R. Weber said 46 per cent.; and A. Smith and W. B. Holmes, 51 per cent. when a stream of burning distilled sulphur is quenched in ice. A. Wigand observed that a sample of plastic sulphur kept for 2 days contained 89·8 per cent. of insoluble sulphur, and when kept for 2 years it contained 29·6 per cent. M. Berthelot regarded the formation of insoluble sulphur to be a kind of *per saltum* change at about 170°, for only a trace appeared at 155°; very little at 163°; 25 per cent. at 170°; 29 per cent. at 185°–205°; and 30 per cent. at 230°, and between 220° and 448°, the amount is fairly constant—over 30 per cent. On the other hand, A. Moitessier found the following percentage amounts of insoluble sulphur were formed by quenching molten sulphur at the indicated temp.:

	143°	148·6°	159·9°	167·4°	179·4°	213·5°	249·9°	284·9°	440°
$S_{\text{insoluble}}$.	0	2·54	7·03	14·77	22·60	27·09	26·31	29·31	30·27

M. Berthelot believed that the reason the amount of insoluble sulphur obtained above 170° falls short of 100 per cent. is because the cooling is not sufficiently rapid. By using a fine stream or a succession of droplets he obtained 61 per cent.; by cooling in ether, 71 per cent.; and if the cooled material be immediately tested with carbon disulphide, 85 per cent.—if the material giving 85 per cent. be extracted next day it gave 45 per cent., and if extracted 2 days afterwards, 39 per cent. On the other hand, A. Moitessier, and A. Smith and W. B. Holmes showed that M. Berthelot erred when he found no insoluble sulphur below 170°; and the method of extraction with carbon disulphide is quite unreliable when the sulphur is in a plastic condition. F. W. Küster obtained 34·2 per cent. of insoluble sulphur at 448°, and K. Schaum, A. Smith and W. B. Holmes, and F. W. Küster symbolized the reaction in the molten sulphur: $S_{\text{insoluble}} \rightleftharpoons S_{\text{soluble}}$. The formation of insoluble sulphur is said to be endothermal because the proportion of the soluble converted into the insoluble form increases with rise of temp. M. Berthelot observed no thermal change at 18°; between 18° and above 160° there was an absorption of heat; and above this temp. the transformation of soluble into insoluble sulphur is exothermal. According to R. Huerre, amorphous, insoluble sulphur is converted into the soluble form by heating it to about 100° with animal or vegetable oil, or with a 10 per cent. soln. of sodium sulphite, or with water alone. M. Berthelot found that the passage of insoluble into soluble sulphur is hindered by keeping it in contact with fuming nitric or sulphurous acid. The presence of a trace of iodine favours the formation of insoluble sulphur. A. Smith and W. B. Holmes also observed that the formation of insoluble sulphur depends on the presence or absence of foreign matters. For instance, hydrogen chloride, air, sulphur dioxide passed through the molten sulphur increases the yield, so does pyrophosphoric acid; solid alkalies, nitrogen, and carbon dioxide lower the yield; hydrogen sulphide greatly retards the transformation of soluble to insoluble sulphur and ammonia inhibits it altogether. A. Smith and W. B. Holmes explained the peculiar behaviour of molten sulphur on the assumption that liquid sulphur can exist in two states which are partially, but only partially, miscible. The one is a pale yellow, mobile liquid which is the normal appearance of molten, rhombic sulphur at temp. below 160°. This is called λ **sulphur**, or S_λ. The other is a brown, viscid liquid called μ-**sulphur**, or S_μ. According to A. Smith and C. M. Carson, the proportion of insoluble S_μ in the equilibrium mixture $S_\lambda \rightleftharpoons S_\mu$ is raised by the addition of iodine. Thus, with two parts of iodine per 100 parts of sulphur, the following results were obtained:

Temperature . . .	150°	165°	220°	310°	448°
$S\mu$ without iodine . .	6·7	14·0	29·4	32·6	34·1 per cent.
$S\mu$ with iodine . . .	13·8	24·1	47·0	54·2	62·7 ,, ,,

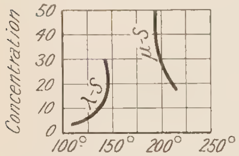


FIG. 7.—Solubility of λ- and μ-Sulphur in Triphenylmethane.

According to A. Smith and W. B. Holmes, a small amount of the latter is formed as soon as the sulphur melts, and it appears in increasing proportions as the temp. rises. The actual proportion is determined by the reversible reaction $S_\lambda \rightleftharpoons S_\mu$. At 160° the S_λ has become a sat. soln. of S_μ, the proportion of the latter at this temp. probably not exceeding 12 per cent. When the temp. is raised beyond this point supersaturation with S_μ ensues and a new phase consisting of S_μ, in which is dissolved a certain proportion of S_λ, arises. According to the phase rule, with one substance, three phases (two liquids and vapour) can coexist only at a definite temp.—the transition point (160°). Hence, above 160° only S_μ, containing amounts of dissolved S_λ which become smaller as the temp. rises, is stable. Rapid heating and the presence or absence of certain foreign substances postpone the transition of S_μ to S_λ and lead to the familiar variations in the temp. at which the sudden viscosity first appears. Conversely, rapid cooling from temp. above 160°, particularly when certain foreign bodies are present, postpones the transition of S_μ to S_λ and hinders or prevents almost entirely the occurrence of the change on which an extensive transformation into S_λ depends. When conditions are favourable, a large proportion of the S_μ may survive to reach the ordinary temp. The chilled product is then a more or less sticky mass which in time partly reverts to soluble sulphur and partly assumes a quasi-solid, difficultly-soluble form. The latter substance is that commonly known as amorphous sulphur. Like all amorphous substances, it is a supercooled state of a liquid, namely, S_μ. The part which reaches the condition S_λ gives brittle, crystalline, soluble sulphur when it solidifies. Curves representing the effects of viscosity, thermal expansion, solubility, vap. press., refractive index, etc., and the temp. of molten sulphur, all take on a new direction on account of the apparent transition occurring near 160°, since λ-sulphur predominates below 160°, and μ-sulphur above that temp. A. Smith and C. M. Carson's observations on the solubility of the two forms in triphenylmethane are illustrated by Fig. 7—the solubility of λ-sulphur increases while that of μ-sulphur decreases with rise of temp. A. Smith and co-workers, and F. Hoffmann and R. Rothe observed that a terrace indicating an absorption of heat, showed on the heating curve, from 161·7° to 167·5°; and, on the cooling curve, an irregularity occurred between 159·5° and 145°. If the cooling liquid be properly stirred to eliminate the effects of undercooling, C. M. Carson observed no irregularity in the rate of cooling;

and the thermal change indicated on the heating curve is greatly influenced by the presence of foreign substances. If molten sulphur be heated rapidly, say 2° per minute, and then chilled, the proportion of μ-sulphur in the product is much below the equilibrium value ; thus,

Temp. before chilling		121°	154°	156°	160°	162°	165°	167°	
μ-Sulphur	observed	0·04	5·4	5·7	—	6·4	7·5	10·3	per cent.
	for equilibrium	3·75	7·5	8·0	10·7	13·5	15·5	16·7	,, ,,

The inference is that when sulphur is rapidly heated, the conc. of the μ-sulphur is about 4 per cent. less than that required for equilibrium up to about 167°—at higher temp. there follows a more rapid formation of μ-sulphur, and the liquid begins to become viscid. If the liquid is heated slowly the μ-sulphur does not differ much from the equilibrium value, a rapid formation of μ-sulphur does not occur, and no break occurs in the heating curve corresponding with a sudden endothermal change. The apparent separation of liquid sulphur into two phases was found by A. Smits, and H. L. de Leeuw to be brought about by the differences in temp. which arise in a column of the liquid, owing to the bad conduction of heat. In reality there is no formation of two phases, the differences in colour being accounted for by the differences in temp. ; and, contrary also to A. Smith and co-workers, H. R. Kruyt assumed a metastable region of partial miscibility. The subject was studied by P. Mondain-Monval and P. Schneider. H. L. de Leeuw showed that there is no satisfactory evidence for the assumption of a region miscibility in the liquid phase. The occurrence of two liquid layers is due to differences in temp., which may amount to 10°–30°, and which is produced by the poor heat-conductivity of molten sulphur. When the thermal conductivity is increased by the introduction of platinum wire or gauze, the phenomenon occurs very indistinctly or not at all. The transition temp. from rhombic to monoclinic sulphur is lowered from 95·45° to about 71° by rapidly cooling sulphur from its b.p. so as to ensure the presence of a large proportion of μ-sulphur. As the proportion of μ-sulphur decreases, the transition temp. rises until it reaches 95·45°, which is regarded as the true unary transition temp. Similarly with the m.p., H. R. Kruyt observed that rhombic sulphur in equilibrium at 90° has a m.p. of 110·9° ; and when the sulphur had attained equilibrium at 65°, the m.p. was 111·4°. These results are in harmony with A. Smits' theory of allotropy which assumes that equilibrium in the solid rhombic phase involves a state of equilibrium between various allotropic components. Let S_r and S_μ denote these two components, the conclusion that the lower the temp. at which the inner equilibrium is established the higher the temp. at which the phase commences to melt is then illustrated graphically by Fig. 8. A. Smits, and H. L. de Leeuw have made tentative, ternary, equilibrium diagrams to include more phases than those indicated diagrammatically in Fig. 8.

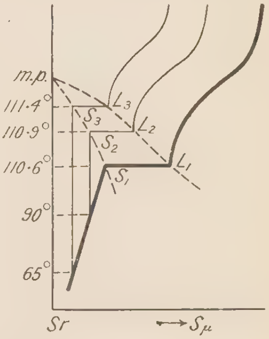


Fig. 8.—Effect of S_μ on the Melting Point of S_γ.

According to J. B. A. Dumas, sulphur which has been fused at various temp. and then quickly cooled in single drops by immersion in cold water, behaves as follows : at 110°–170°, it solidifies to a yellow mass the colour of ordinary sulphur ; at 190°, it is first soft and transparent, but quickly becomes brittle and opaque, and acquires the colour of ordinary sulphur ; at 220°, it becomes soft, transparent, and brownish-yellow ; at 230°–260°, it becomes soft, ductile, transparent, and of a reddish colour ; at the b.p., it becomes very soft, transparent, and reddish-brown. All depends on the temp. ; the time of fusion has no perceptible influence. If sulphur be poured into water in large masses, the inner portions which cool slowly solidify as ordinary sulphur ; rapid cooling prevents crystallization. According to J. Fritzsche, when viscid sulphur is dropped into oil it becomes covered with well-developed crystals and loses its transparency. C. J. St. C. Deville observed that the sp. gr. of recently-fused sulphur was 1·9578, and owing to *le movement dans les densités*, this constant became 2·0498 in 20 months. This metastability was discussed by E. Cohen. H. V. Regnault observed that if the plastic sulphur be kept at 93° its temp. rises to 110° as it passes into the crystalline state. The rate of crystallization was found by D. Gernez to be a maximum for sulphur which had been heated to 170°; P. Duhem, A. Smith and W. B. Holmes, and G. Tammann found that the rate of crystallization varies proportionally with the degree of undercooling—Fig. 8; and D. Gernez, that when the undercooled liquid is seeded, the velocity of crystallization is smaller with rhombic than with monoclinic sulphur, being 7·50 secs. in the former case and 0·20 sec. in the latter case with sulphur kept 15 mins. at 129·5°, and then cooled to 80·9°. J. H. Kastle and W. P. Kelley found that the rate of change of plastic into crystalline sulphur varies with the temp. to which the sulphur was heated before being poured into water, and also with the temp., for the higher the temp. at which the sulphur is kept, the faster the crystallization. Light, amber-coloured, plastic sulphur crystallizes easily, while the reddish-brown varieties crystallize more slowly. The velocity of the change of plastic into crystalline sulphur begins comparatively rapidly, about 10 per cent. of the total change takes place in the first 30 minutes, and then gradually diminishes. This gradual decrease in the rate of crystallization indicates that several molecular forms are present in the supercooled liquid, some of which change to the crystalline variety of the element more rapidly than others. The presence of ammonia, alcohol, and bromine accelerates the crystallization. The slopes of the curves, Fig. 9, indicate the rates of crystallization in contact with water and in contact with a 0·1N-soln. of iodine. G. Linck and E. Korinth studied the crystallization of sulphur and the formation of diffusion rings. H. Freundlich and F. Oppenheimer found that sulphur sols lower the velocity of crystallization of water.

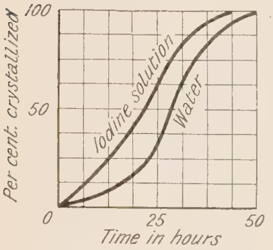


Fig. 9.—Speed of Crystallization of Plastic Sulphur, under Water, and under a $\frac{1}{10}N$-solution of Iodine.

J. B. A. Dumas gave 108°–109° for the f.p. of sulphur. C. M. Marx showed that during the freezing at 99°–100° the temp. rises to 109°–110°; M. L. Frankenheim, that when sulphur cooled to 105°–108° begins to freeze, the temp. rises to 112°, and there remains until all is solidified. B. C. Brodie, R. F. Marchand and T. Scheerer, M. Faraday, and A. Bellani also made observations on this subject. D. Gernez showed that sulphur always freezes below its m.p., and this is not because of the effects of undercooling. D. Gernez, A. Smith and W. B. Holmes, and J. Dussy showed that the f.p. of molten sulphur is not constant since it depends on the temp. at which the sulphur has been heated, for the fused sulphur is a homogeneous mixture of soluble and insoluble sulphur. R. F. Marchand gave 113° for the f.p.; H. V. Regnault, 113·6°; and D. Gernez found 117·4° for sulphur which had been heated to 121°; 113·4°, when heated to 144°; 112·2°, when heated to 170°; and 114·4°, when heated to 200°–447°. A. Smith and W. B. Holmes extrapolated the results for rhombic sulphur free from the insoluble form, and gave for the f.p. of idealized sulphur 119·25°. H. R. Kruyt said that mixed crystals of μ- and λ-sulphur separate when a homogeneous liquid mixture is allowed to cool, but A. Wigand showed that pure crystalline λ-sulphur separates out first. E. Beckmann and co-workers attributed the absence of a sharp m.p. with sulphur to the presence in the liquid of molecules of different degrees of complexity.

In general, as shown by P. Duhem, H. W. B. Roozeboom, and W. D. Bancroft, substances which freeze below their m.p. are capable of existing in two solid forms which melt at different temp. and form liquid systems of identical constitution in which the liquid states of the two forms can coexist in equilibrium. The two forms of liquid sulphur : λ-sulphur⇌μ-sulphur, is taken to be a case of *dynamic allotropy* because the change is reversible, there is no transition temp., and the amount of each form present in the system, when in equilibrium, is determined by the temp. The two forms are also called *dynamic isomerides*. In Fig. 10, *A* may be regarded as the f.p. of λ-sulphur ; *B*, that of μ-sulphur ; and *C*, that of the eutectic. The line *AC* represents the effect of μ-sulphur on the f.p. of λ-sulphur. Here *C* and *B* are unknown ; but the line *AC* has been traced as far as 112·45° and 5·3 per cent. of μ-sulphur. *DG* represents the proportion of the two dynamic isomerides in the liquid phase at different temp., and *D*, 114·5°, is the f.p. in a system in equilibrium with 3·7 per cent. of μ-sulphur at the time of freezing. Hence, W. D. Bancroft would call this the *natural freezing-point* of sulphur—*vide supra*, L_1S_1, Fig. 8. It is really a triple point at which the three phases—liquid S_λ and S_μ ; solid monoclinic sulphur ; and vapour of sulphur—are in equilibrium. At the b.p. there is 34·1 per cent. of μ-sulphur in equilibrium with the liquid ; and C. M. Carson found :

	121°	155°	157°	159·25	160°	161°	163°	165°
μ-Sulphur . . .	3·75	7·7	8·2	10·4	11·5	12·5	13·9	15·5

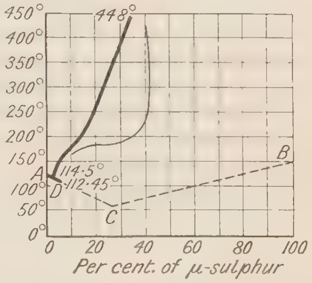


FIG. 10.—The Effect of Temperature on the Equilibrium Proportions of Sλ and Sμ.

D. L. Hammick and co-workers obtained the results summarized by the light curve, Fig. 10.

B. Lange and W. Cousins also showed that in the molten state the sulphur molecules are depolymerized, say $S_8 \rightleftharpoons 2S_4$ and $2S_4 \rightleftharpoons S_2 + S_6$. A. H. W. Aten showed that if a soln. of rhombic sulphur in sulphur monochloride, sat. at ordinary temp., be heated to about 150°, and then cooled, much more sulphur can be dissolved by the liquid. Thus, mixtures of λ-sulphur and sulphur monochloride in sealed tubes were heated to 100° for several hours and quickly cooled. Representing compositions by the number of gram-atoms of sulphur per 100 gram atoms of $S + S_2Cl_2$ in the original mixture, the sat. soln. at the temp. named contained :

Original . . .		0	28·7	49·9	79·4	80·1	90·1	98·0
Sat. soln. .	−60°	11·6	31·9	42·9	65·2	66·1	—	—
	0°	36·1	47·4	56·0	72·0	71·6	80·5	—
	25°	53·5	62·0	66·4	—	—	—	93·4

Similar results were obtained with mixtures previously heated to 50°, 75°, and 125°. It is inferred that this is not due to the formation of μ-sulphur from λ-sulphur, for the solubility of the former is very small at ordinary temp., and if soln. be sat. with this form of sulphur at a higher temp., it readily separates out on cooling. It was also shown that the phenomenon is not due to the combination of sulphur with sulphur monochloride ; and it was inferred that the phenomenon is a result of the formation of another form of liquid sulphur -**π-sulphur.** Indications of the formation of π-sulphur, in the absence of sulphur monochloride, were obtained, for if sulphur be heated alone to 125° and rapidly cooled, its solubility in sulphur monochloride is distinctly greater than that of the unheated rhombic sulphur. Thus, samples of sulphur were heated to the indicated temp., and rapidly cooled. The number of gram-atoms of sulphur dissolved per 100 gram-atoms of $S + S_2Cl_2$ were as follows : Unheated sulphur, 53·5 ; mixture of rhombic and amorphous sulphur, 54·5 ; rhombic sulphur heated to 125°, 56·0 to 58·5 ; rhombic sulphur heated to 165°—freshly prepared, 60 ; kept an hour, 59·5 ; kept 24 hrs., 57·5 ; and kept 8 days, 53·2. Sulphur which has been heated to 170° and chilled contains as much π-sulphur as when heated to 445° and chilled. The π-sulphur dissolved in sulphur monochloride quickly changes into μ-sulphur. Similar results were obtained with toluene as a solvent. The increased solubility of sulphur which has been heated to 170° is due to the π-sulphur which is present as a mixture, or as a solid soln. with λ-sulphur. Soln. containing π-sulphur are all yellow; a carbon disulphide soln. with 18 at. per cent. π-sulphur is as yellow as a conc. aq. soln. of potassium chromate. When a carbon disulphide soln. of λ- and π-sulphur is cooled to —80°, the whole of the λ-sulphur separates out leaving only π-sulphur in soln. If this soln. be evaporated, white, amorphous μ-sulphur remains. If the solvent is removed at —80°, by a reduction of press., sulphur soluble in carbon disulphide with a small residue of μ-sulphur is formed. When soln. of λ-sulphur and of mixed π- and λ-sulphur are exposed to a strong light, less μ-sulphur is precipitated with the mixed soln. than in the case of the soln. of λ-sulphur. If π-sulphur is really μ-sulphur more should have been precipitated from the mixed soln. The relative proportions of the three forms of sulphur can be determined in a given sample of sulphur; for, if solid sulphur be digested with carbon disulphide, the μ-sulphur remains undissolved; and if the mixed soln. be cooled to —80°, the λ-sulphur is alone precipitated. Sulphur which has been heated to the temp. indicated was found to contain the following proportions of these three forms:

	120°	130°	140°	160°	170°	180°	220°	445°
μ-Sulphur	96·4	95·4	93·7	89·2	80·9	73·1	62·7	59·1
π-Sulphur	3·5	4·3	5·0	6·7	5·8	6·5	5·3	4·0
λ-Sulphur	0·1	0·3	1·3	4·1	13·3	20·4	32·2	36·9

The amount of π-sulphur is a maximum in that which has been heated to 180°; the quantity of μ-sulphur decreases as the temp. rises from 120° to 445°—the greatest rate of decrease is between 170°–180°; the proportion of λ-sulphur increases with rise of temp. The change of π- to μ-sulphur is at first very rapid, but the velocity quickly decreases and becomes very small when only a little π-sulphur is present. The effect of ammonia on the equilibria: $S_\mu \rightleftharpoons S_\pi \rightleftharpoons S_\lambda$, is to increase the transformation of the π-sulphur more than it does μ-sulphur. A. Smith and co-workers found that ammonia accelerates the formation of λ-sulphur from μ-sulphur, while iodine acts in the converse way. A. H. W. Aten found that iodine has no effect on the transformation $S_\pi \rightarrow S_\mu$. The soft variety of ordinary μ-sulphur is really a mixture of all these varieties, but with the proportion of λ-sulphur very small. In agreement with A. H. W. Aten, E. Beckmann and co-workers hold that it is π-sulphur, not μ-sulphur, which is the cause of the depressed or natural f.p. of sulphur. Sulphur with its f.p. 114·5° has 2·78 per cent. of π-sulphur, not 3·6 per cent. of μ-sulphur, as A. Smith and co-workers supposed. E. Beckmann and co-workers showed that amorphous sulphur prepared in a variety of ways has no effect on the f.p., but this sulphur is readily transformed into a mixture of λ- and π-sulphur in the same proportions as is present in the fused mass. If the fusion is rapidly cooled after the addition of the μ-sulphur, only about 24 per cent. of the added sulphur is still insoluble in carbon disulphide. When added to a fused mass having a lower f.p. than 114·5°, μ-sulphur has no effect, but when added to one having a higher f.p., it has the effect of lowering it towards the natural f.p., indicating that at the higher temp. relatively more π-sulphur is formed from the μ-sulphur. When μ-sulphur is heated, it shows no sharp m.p., but, having reached 120°, it has at once the natural f.p. 114·5°. If a mixture of rhombic sulphur with about 5 per cent. μ-sulphur is melted, it has a f.p. about 2° lower than that of a sample of rhombic sulphur similarly treated, indicating that under these conditions, the μ-sulphur decomposes into 23 per cent. π-sulphur and 77 per cent. λ-sulphur. When a sample of π-sulphur was added to a sample of natural sulphur, it lowered the f.p. slightly, indicating, however, only about 4·6 per cent. π-sulphur in the preparation. Both rhombic and monoclinic sulphur raise the f.p. of natural sulphur by increasing the proportion of λ-sulphur.

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§ 6. The Physical Properties of Sulphur

The **colour** of native sulphur may be straw-yellow, honey-yellow, yellowish-brown, greenish, reddish, or yellowish-grey, and even black owing to the presence of carbonaceous matter. C. F. Schönbein[1] found that, at −50°, α-sulphur, and flowers of sulphur are almost colourless, and at 0° it is paler than at ordinary temp.; whilst at 100°, it is deep yellow. R. Engel's trigonal sulphur is orange-yellow. The colour of colloidal sulphur and of sulphur compounds has been discussed above. Precipitated sulphur may be white or yellow according to the grain-size of the particles. Plastic sulphur is brown, and the darkening of the colour which occurs when sulphur is heated has been previously discussed. J. L. Howe and S. G. Hamner said that the colour of the vapour varies with the temp., being orange-yellow—like N-$K_2Cr_2O_7$—just above the b.p. The colour darkens as the temp. rises until it becomes deep red—resembling that of a soln. of ferric thiocyanate. The red is most intense at about 500°; the colour then becomes paler and paler as the temp. rises until, at 634°, it is straw-yellow. A. N. Dey and S. Dutt studied the effect of sulphur on the colour of compounds with sulphur.

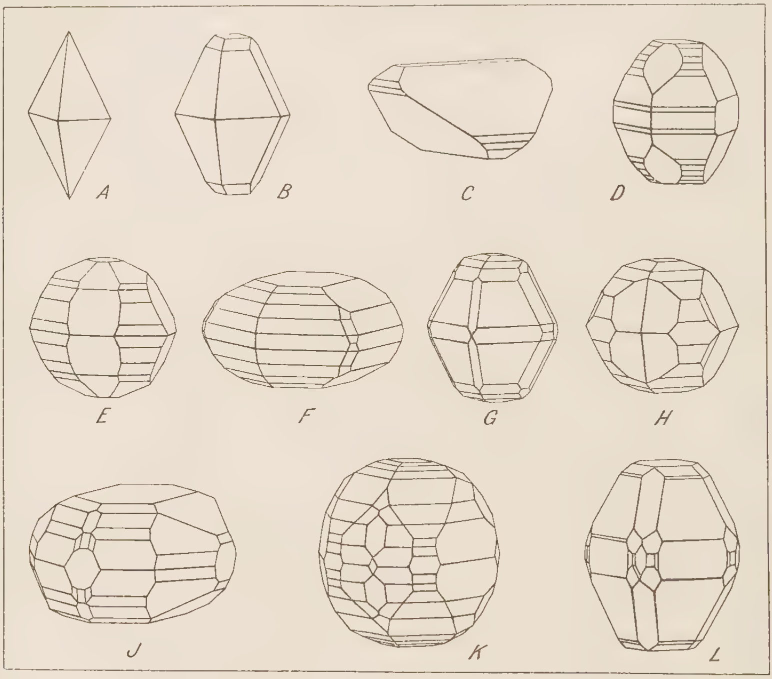


FIG. 11.—Forms of Crystals of Rhombic or α-Sulphur.

Sulphur may occur massive, in powder, as incrustations, in stalactitic or stalagmitic forms, and in spherical or reniform shapes. The crystals of rhombic sulphur were obtained, in 1782, by B. Pelletier[2] by evaporating a soln. of sulphur in turpentine. J. Alexander observed crystallitic transition forms between colloidal and crystalline sulphur deposited from soln. in carbon disulphide in the presence of Canada balsam; they commonly occur in acute pyramids, sometimes thick tables parallel to the (001)-faces; and also with a spheriodal habit. G. Aminoff made observations on this subject; and G. Linck and E. Korinth noted the formation of diffusion rings and globulites in the evaporation of a soln. of sulphur in carbon disulphide thickened with rubber or Canada balsam. The angles were described by J. B. L. Romé de l'Isle in 1783; and by R. J. Haüy in 1801. The rhombic bipyramidal crystals of α-sulphur were found by A. Brezina to have the axial ratios $a:b:c=0{\cdot}8108:1:1{\cdot}9005$; N. von Kokscharoff gave $0{\cdot}81309:1:1{\cdot}90339$; A. Scacchi, $0{\cdot}813:1:1{\cdot}906$; V. Goldschmidt, $0{\cdot}8138:1:1{\cdot}9051$; L. Bombicci, $0{\cdot}81264:1:1{\cdot}90880$; A. Arzruni, $0{\cdot}81365:1:1{\cdot}89863$; and

G. Tschermak, 0·8130 : 1 : 1·9037. Observations were also made by H. Baumhauer, K. Beierle, F. R. Bichowsky, C. Brame, K. Busz, H. Buttgenbach, E. S. Dana, L. Fletcher, G. Flink, P. Gaubert, P. Groth, F. Hessenberg, A. Johnsen, A. G. Kenngott, R. Köchlin, A. Maier, E. Manasse, E. Mitscherlich, G. A. F. Molengraaf, W. Muthmann, T. Nicolau, P. Niggli, L. Pasteur, A. Pelikan, C. Perrier, E. Quercigh, G. vom Rath, V. Rosicky, A. Scacchi, A. Schrauf, E. C. Schröder, S. J. Shand, A. Simek, E. Tacconi, W. Vernadsky, W. H. Weed and L. V. Pirsson, V. R. von Zepharovich, and R. von Zeynek. The fundamental form of the crystals is shown at *A*, Fig. 11 ; *B* is one of the principal forms of the crystal ; *C*, by G. vom Rath, represents a crystal from Racalmuta ; *D*, by K. Busz, is from Wheatley Mines ; *E*, by K. Busz, is from Monte Poni ; *F*, by A. Brezina, is from Oker ; *G*, by A. Simek, is from Kostaïnika ; *H*, by K. Busz, is from Wheatley Mines ; *J*, and *K*, by A. Simek, are from Kostaïnika ; and *L*, by F. R. von Bichowsky, is an unusual artificial crystal. F. Ranfaldi discussed the crystallographic data of rhombohedral sulphur produced by volcanic eruptions. According to G. vom Rath, **twinning** occurs about the (101)-plane ; and symmetrical penetration twins sometimes occur ; twinning also occurs about the (011)-plane, and rarely about the (110)-plane. The **cleavages** on the (001)-, (110)-, and (111)-faces are imperfect. G. Wulff discussed the cleavage of sulphur crystals. A. des Cloizeaux gave for the **optic axial angles** $2H_a$=103° 18′ for red-light, 104° 12′ for yellow-light, and 106° 16′ for blue-light at 17° ; $2V$=69° 2′ for red-light, 69° 5′ for yellow-light, and 69° 13′ for blue-light. A. Schrauf gave for Na-light at 8°, $2V$=69° 4′ 50″, $2G$=98° 19′ 4″, and $2H$=103° 3′ 55″ ; at 20°, $2V$=68° 58′ 0″, $2G$=97° 58′ 9″, and $2H$=103° 6′ 45″ ; and at 30°, $2V$=68° 53′ 2″, $2G$=97° 40′ 44″, and $2H$=103° 9′ 6″ ; and for Tl-light at 8°, $2V$=68° 53′ 48″, $2G$=99° 7′ 11″, and $2H$=103° 54′ 24″ ; at 20°, $2V$=68° 46′ 11″, $2G$=98° 44′ 51″, and $2H$=103° 55′ 53″ ; and at 30°, $2V$=68° 39′ 17″, $2G$=98° 23′ 13″, and $2H$=103° 54′ 4″. V. Rosicky, S. Kreutz, T. Wada, L. Bombicci, G. Aminoff, and S. J. Shand investigated the **corrosion figures** and the symmetry of the rhombic crystals. A. von Fischer-Treuenfeld described the ring and dendritic structures which have been observed when thin films of liquid sulphur are allowed to crystallize. The effects are ascribed to the action of capillary forces, in virtue of which the crystalline aggregates exert an attractive force on the neighbouring liquid. Other forms have been indicated previously in connection with the freezing of molten sulphur.

The tabular or acicular monoclinic crystals of β-sulphur were found by A. Mitscherlich to have the axial ratios $a:b:c$=0·9958 : 1 : 0·9998, and β=95° 16′. W. Muthmann gave 0·99575 : 1 : 0·99983, and β=95° 46′. Two forms of the prismatic crystals are shown in Fig. 13. Twinning occurs about the (100)- or the (011)-plane. This subject was discussed by E. Mitscherlich, A. T. Kupffer, J. J. Bernhardi, F. A. Quenstedt, R. Brauns, and P. Gaubert. The (110)-cleavage is distinct. E. Kordes said that monoclinic sulphur separates from a soln. of sulphur in naphthalene or iodine. The so-called *Daiton-sulphur* from the volcano of Daiton, Japan, was supposed by M. Suzuki, and T. Wada to occur in monoclinic prisms, but R. Ohashi showed that the crystals are more probably rhombic. W. Muthmann gave for the

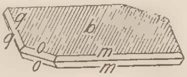


FIG. 12.—Crystal of γ-Sulphur or *le soufre nacre.*

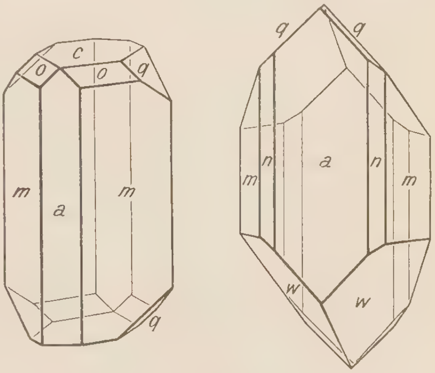


FIG. 13.—Forms of Crystals of Monoclinic or β-Sulphur.

axial ratios of the monoclinic plates of γ-sulphur, Fig. 12, $a:b:c=1·0609:1:0·7094$, and $\beta=91°$ 47. The angles $m:m=56°\ 4'$; $q:q$ 40° 24′; $o:o=60°\ 0'$; $q:m=88°\ 16'$; $o:q=146°\ 43'$; and $o:m=124°\ 45'$. The crystals were also examined by W. Salomon, and P. Gaubert. W. Muthmann also showed that the hexagonal plates of δ-sulphur, Fig. 14, are probably monoclinic, with the crystal angles $a:c=76°\ 30'$; $w:c=76°$; and $a:w=65°$. R. Engel's variety—ϵ-sulphur—was found by C. Friedel to crystallize in orange-yellow plates belonging to the trigonal system. W. Schneider examined the piezoelectric effect. W. H. Bragg made some observations on the **X-radiogram** of rhombic sulphur. H. Mark and E. Wigner found that the space-lattice of the rhombic bipyramids has the dimensions $a=10·61$ A., $b=12·87$ A., and $c=24·56$ A.—values twice as large as those obtained by W. H. Bragg, who gave $a=5·23$ A., $b=6·43$ A., and $c=12·23$ A. The elementary cell is estimated to contain 128 atoms, of which 16 are geometrically related to form the crystal molecule. The centres of gravity of these groups form a rhombic diamond lattice. H. Whitaker[3] said that nacreous sulphur forms six-sided plates with 3 pairs of opposite sides parallel. The colours are due to interference. The plates gradually disintegrate into the more stable octahedral form.

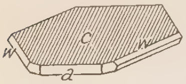


Fig. 14.—Crystal of δ-Sulphur.

In 1690, R. Boyle gave 2·00 for the **specific gravity** of sulphur vivum, and 1·98 for that of a "very fine" sample from Germany. For native sulphur, A. le Roger and J. B. A. Dumas gave 2·086; C. J. B. Karsten, 2·05001; R. F. Marchand and T. Scheerer, 2·062 to 2·070; H. Kopp, 2·069; G. vom Rath, 1·97; O. Silvestri, 2·001 to 2·009; and 2·00630 at 26°; G. Pisati, 2·0748 at 0°/4°; V. Goldschmidt, 2·069 at 18°; G. Vicentini and D. Omodei, 2·0748 at 0°; F. R. von Bichowsky, 2·01; C. J. St. C. Deville, 2·070; and C. Brame, 2·0757; F. Mohs, 2·072; and A. Schrauf, 2·06665 at 16·75°/14°; and for the sp. gr. of pieces of sulphur 2·06890 at 7·81°, and 2·07019 at 23·28°; 2·06939 at 8·25°, and 2·07066 at 26·05°; 2·06974 at 8·64°, and 2·07085 at 26·32°; and 2·06984 at 8·27°, and 2·07057 at 25·22°. W. Spring gave for sulphur from Sicily, 2·0788 at 0°, 2·0688 at 20°, 2·0583 at 40°, 2·0479 at 60°, 2·0373 at 80°, and 2·0220 at 100°. For roll sulphur, M. J. Brisson gave 1·9907; J. Dalton, 1·98–1·99; C. W. Böckmann, 1·868; and T. Thomson, 1·9777 to 2·0000. For sulphur crystallized from fusion, C. J. B. Karsten gave 1·9889. J. K. Gehler gave for flowers of sulphur, 2·086; and L. Playfair and J. P. Joule, 1·913. J. S. E. Julia-Fontenelle gave for crystalline sulphur, 1·898; A. Breithaupt, 1·989; L. Playfair and J. P. Joule, 2·010; and L. Maquenne, 2·041 to 2·049; G. Bischof gave 1·927 for sulphur crystallized from soln.; R. F. Marchand and T. Scheerer, 2·0518; C. J. St. C. Deville, 2·063; E. Petersen, 2·01 in pieces and 1·99 in powder; L. M. Arons, 2·07; L. Hecht, 2·06; and W. Spring, 2·0477 at 0°, 2·0370 at 20°, 2·0283 at 40°, 2·0182 at 60°, 2·0014 at 80°, and 1·9756 at 100°. E. Madelung and R. Fuchs gave 2·0709. I. I. Saslowsky gave 2·07 for the sp. gr. of sulphur at room temp., and 15·5 for the at. vol. C. del Fresno studied this subject.

For soft sulphur, fused and poured into cold water, G. Osann gave 2·027; R. F. Marchand and T. Scheerer, 1·957 to 1·961; C. J. St. C. Deville, 1·919 to 1·928; and C. Brame, 1·87 to 1·9319; while for waxy sulphur, L. Playfair and J. P. Joule gave 1·921; and W. M. Müller gave 1·87 for amorphous yellow sulphur, and 1·91 to 1·93 for brown amorphous sulphur. For the amorphous precipitated sulphur, L. Troost and P. Hautefeuille gave 2·046; and E. Petersen, 1·87. M. Töpler gave for the sp. gr. of insoluble amorphous sulphur—possibly μ-sulphur—1·849 at 40° to 50°; A. Wigand gave 1·878 for the sp. gr. of plastic sulphur, and 1·892 for insoluble amorphous sulphur; while W. Spring gave for insoluble sulphur 1·9556 at 0°; 1·9496 at 20°; 1·9041 at 40°; 1·9438 at 60°; 1·9559 at 80°; and 1·9643 at 100°. M. Töpler gave for the sp. vol., referred to unit vol. of liquid sulphur at 120°, 0·963 at 30°; 0·974 at 60°; 0·995 at 120°; 1·001 at 140°; 1·007 at 160°; 1·014 at 180°; and 1·021 at 200°. L. Playfair and J. P. Joule gave 1·801 to 1·815 for molten sulphur; and W. Ramsay, 1·4578 to 1·5130—mean 1·4794 at 446°. G. Vicentini and

D. Omodei gave 1·8114 for the sp. gr. of sulphur at its m.p. 113°; H. Kopp. 1·892; G. Osann, 1·927; and L. M. Arons, 1·811. For the sp. vol. of liquid sulphur, referred to unity at 120°, M. Töpler gave 0·933 at—20°; 0·943 at 0°; 0·951 at 20°; 0·960 at 40°; 0·969 at 60°; 0·979 at 80°; 0·9889 at 100°; 1·0000 at 120°; and 1·0117 at 140°. A. M. Kellas found for the sp. gr., D,

	115·1°	134·0°	145·5°	158·5°	161·0°	178·3°	357·0°	445·0°
D .	1·8094	1·7921	1·7807	1·7710	1·7704	1·7652	1·6565	1·5994

The results are plotted in Fig. 15. The break beginning at about 160° is followed by a complete alteration of alignment.

As shown by A. Breithaupt, the sp. gr. of β-sulphur is less than that of rhombic α-sulphur. R. F. Marchand and T. Scheerer gave 1·957; C. J. St. C. Deville, 1·958; B. Rathke, 1·960; and E. Petersen, 1·94. M. Töpler gave 1·957 at 25·15°, 1·954 at 31°, 1·950 at 41° to 45°, and 1·802 at 120°; and the sp. vol. was 0·915 at 0°; 0·919 at 20°; 0·924 at 40°; 0·929 at 60°; 0·935 at 80°; and 0·941 at 100°. R. Engel gave 2·135 for the sp. gr. of trigonal or ϵ-sulphur.

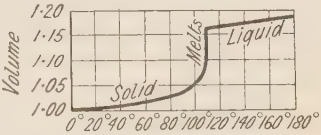


FIG. 15.—Volume Changes on Heating from 0° to 180°.

The best representative values for the sp. gr. are 2·07 for α-sulphur; 1·96 for β-sulphur; and 1·92 for amorphous sulphur. M. Delepiné studied the substitution of sulphur for oxygen in various organic compounds as regards density; he found that with the exception of hydrogen sulphide and thiophosphoryl chloride, sulphur compounds are heavier than their oxygen analogues. With the substitution of several oxygen atoms by sulphur atoms, the differences between the densities of the corresponding compounds increase, but this effect disappears as the mols. become more complex. Whilst oxygen ethers are generally less dense than the isomeric alcohols, the sulphur ethers have about the same density as the isomeric mercaptans, and the same is true for isomerides of the types X.CS.OR and X.CO.SR, but for compounds of the types X.CS.N: and X.CN.S. the former have higher densities than the latter. I. I. Kanonnikoff observed that with 32 sulphur compounds, free sulphur has the mol. density 121·2, and this is also the value in those of its compounds in which it acts as a bivalent element. When the valency increases, the mol. density increases by multiples of 23·2, so that in the quadrivalent condition, the value is 144·4, and in the sexavalent state, 167·6. In compounds of different types, the mol. density of sulphur shows a behaviour resembling that of oxygen in analogous compounds; thus the value for oxygen or sulphur existing in the form C.O.C. or C.S.C. is 7·74 less than the value for the free element, whilst in C : S or C : O, the value is increased by 4·84.

H. Macagno[4] measured the sp. gr. of soln. of sulphur in carbon disulphide at 15°; expressing the results in parts of sulphur per 100 parts of solvent, he obtained:

Sulphur . .	0	0·2	1·2	5·1	10·2	20·1	30·2	37·2
Sp. gr. . .	1·271	1·272	1·276	1·292	1·313	1·354	1·380	1·391

If D denotes the sp. gr. at 15°; and d, the sp. gr. at $\theta°$, then $D=d+0{\cdot}0014(\theta-15)$. C. Montemartini and L. Losana found that the sp. gr.–temp. curve of soln. of sulphur in nitrobenzene changes direction at about 90°, and has an arrest at 115°; while 3 and 20 per cent. soln. in acetamide have arrests at 42° and 65° respectively. G. J. Pfeiffer obtained for soln. with the following percentage amounts of sulphur, the following sp. gr. at 15°/4°:

Sulphur . .	0	0·2	0·4	2·0	5·0	10·0	15·0	20·0
Sp. gr. . .	1·2708	1·2717	1·2727	1·2802	1·2949	1·3195	1·3450	1·3709

Some observations on the **specific volume** of the different forms of sulphur have been already recorded. Fig. 15 represents the vol. changes which occur when sulphur is heated from 0° to 180° when the vol. at 0° is regarded as unity. M. Töpler[5] gave 5·5 per cent. expansion. T. E. Thorpe calculated the **atomic volume** of the sulphur atom in hydrogen sulphide, and thiocarbonyl chloride to be 28·4 ; in sulphur monochloride and thionyl chloride, 22·6 ; in carbon disulphide one sulphur atom has the at. vol. 22·6 and the other, 28·6. H. Kopp gave respectively 22·6 and 28·6 ; and I. Traube, 10 to 11·5 and 15·5. H. Buff gave 27·8 for bivalent sulphur, 22·6 for quadrivalent sulphur, and 12 for sexivalent sulphur. I. I. Saslavsky, F. Schuster, A. F. Hallimond, S. Sugden, and E. Donath and J. Mayrhofer made some observations on this subject. W. Ramsay's result for the sp. gr. of sulphur at its m.p. gives 21·6 ; or for the sp. vol. 0·6757. E. Petersen calculated 15·9 for the at. vol. of α-sulphur ; 16·4 for β-sulphur ; and 17·1 for μ-sulphur. According to I. Traube, the relative vapour density of sulphur vapour in the neighbourhood of its b.p. is in agreement with Trouton's rule when special assumptions are made with respect to the complexity of the molecules of the vapour. F. Exner found that 1 c.c. of the vapour weighs 0·00575 grm., and of this vol. 0·00105 c.c. is occupied by matter. H. G. Grimm and H. Wolff calculated for the **atomic radius** $1{\cdot}059\times10^{-8}$ to $1{\cdot}114$ 10^{-8} cm. ; F. Schulze 1·477 (oxygen unity). W. L. Bragg, and M. L. Huggins calculated 1·02 A. for the atomic radius ; L. S. Ramsdell, 1·04 A. ; B. Cabrera, 1·01 A. to 1·13 A. for the at. radius of S'' ; A. Ferrari, 1·20 A. ; W. P. Davey, 1·03 A. to 104 A. ; and W. F. de Jong and H. W. V. Willems, 1·04 A. Observations were made by V. M. Goldschmidt, L. Pauling, and E. T. Wherry from which it follows that the effective at. radius for sexivalent sulphur atoms is 0·29 to 0·34 A. ; for neutral sulphur atoms, 1·02 to 1·04 A. ; and for bivalent negative sulphur atoms, 1·74 to 1·84 A.

About a century ago, the **vapour density** of sulphur at its b.p. was found by J. B. A. Dumas,[6] and E. Mitscherlich to be between 6·5635 and 6·9. J. von Liebig, in his letters to J. J. Berzelius, mentioned that he had obtained very variable results which he did not publish. H. St. C. Deville and L. Troost gave 2·23 between 860° and 1040° ; this corresponds with 2·21 calculated for S_2 ; A. Bineau, 2·7 between 714° and 743° ; and 2·36 between 8·34° and 1162° ; and L. Troost, 6·7 at 440° and 104 mm. press., 6·3 at 60 mm. press., and 3·0 at 665°. H. Biltz said that the vap. density below 800° is greater than the value corresponding with S_2, and although the value 7·8 was obtained at 468°, the values in this region of temp. are not constant. W. Ramsay suggested that the mol. of sulphur at ordinary temp. approaches S_8 ; that when the temp. is raised, the complex mol. dissociates into S_2 and S_6 ; and that at still higher temp., the S_6-molecule dissociates into S_2-molecules. A. Krause and V. Meyer found at 19·5°–20°, in an atm. of nitrogen at 743 mm. press., the mol. approximates S_7 ; and J. F. C. Schall, S_8. W. T. Cooke made some observations of the vap. density of sulphur in argon, etc. H. Biltz showed that even at the b.p. some S_8-mols. are dissociated into S_2-mols., and at 900°, the dissociation $S_8 \rightleftharpoons 4S_2$ is complete. He said that there is no evidence of the existence of S_6-mols. because the vap. density steadily decreases with a rise of temp. The vap. density becomes constant only above 900°. G. Preuner and W. Schupp's results are illustrated by Fig. 16 ; they could not reconcile their observations with the assumption that only S_8- and S_2-mols. are present, but inferred that S_8-, S_6-, and S_2-mols. are present. G. Preuner discussed the possibility of there being S_4-mols. also present. O. Bleier and L. Kohn found that at temp. between 192° and 310°, and at a low press., the results approximate asymtotically to S_8 as the press. is increased ; and H. Biltz and G. Preuner also observed that at low temp., the results approach S_8 as a maximum value. I. Brockmöller represented the reaction $3S_8 \rightleftharpoons 4S_6$; $S_6 \rightleftharpoons 3S_2$; and $S_8 \rightleftharpoons 4S_2$. If the bracketed terms represent partial press., $[S_6]^4 = K_1[S_8]^3$; $[S_2]^3 = K_2[S_9]$; and $[S_2]^4 = K_3[S_8]$, so that :

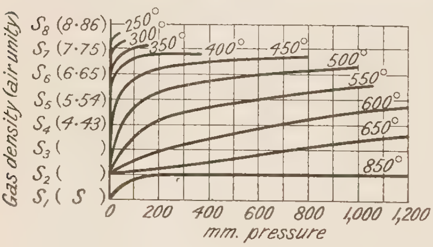


FIG. 16.—Isotherms for the Vapour Densities of Sulphur at different Pressures.

	300	400°	500°	600°	850°
K_1 . . .	3·6	2×10^2	4×10^3	4×10^4	2×10^6
K_2 . . .	$3·4\times10^{-4}$	2·0	$1·3\times10^3$	$1·7\times10^5$	9×10^8
K_3 . . .	$3·6\times10^{-5}$	14·7	$2·37\times10^5$	$3·22\times10^8$	$1·10\times10^{14}$

G. Preuner and W. Schupp found for the vap. press. in mm. of mercury, and the calculated values for the partial press. $[S_8]$, $[S_6]$, and $[S_2]$. The results are shown graphically:

	100°	150°	200°	250°	300°	350°	400°	450°
p	0·0085	0·23	2·26	12·0	48·0	128·0	378·0	828·0
$[S_8]$	0·0075	0·1915	1·74	8·4	30·2	70·5	183·0	346·0
$[S_6]$	0·0010	0·0385	0·52	3·6	17·8	56·5	187·0	450·0
$[S_2]$	—	—	—	—	—	1·28	7·2	31·6

in Fig. 16. A. Scott, and V. and C. Meyer found that the vap. density at 1560° is in agreement with S_2; and likewise, H. Biltz and V. Meyer, at 1719°. H. von Wartenberg found a mol. wt. of 50 at 2070°, showing that at this temp. there is an appreciable dissociation $S_2 \rightleftharpoons 2S$. Assuming that the S_6-mols. represent μ-sulphur insoluble in carbon disulphide, the proportion of S_μ-mols. in sat. sulphur vapour, calculated from the observed densities, is in agreement with the values determined by J. Gal, but not with those of H. R. Kruyt. It is possible that at press. below 30 mm., S_1-mols. are also contained in the vapour. From observations on the explosion of hydrogen sulphide with electrolytic gas, H. Budde was able to show that in all probability the S_2-mols. dissociate into single atoms above 1800°; and that at 2450°, and atm. press., about one-half the vapour is dissociated: $S_2 \rightleftharpoons 2S$. This reaction was studied by D. Alexéeff. H. Staudinger and W. Kreis tried unsuccessfully to isolate solid S_2 by chilling the gas from 1000° to −190°. V. Kistiakowsky discussed the mol. constitution of the liquid. K. Stock found that **active sulphur** can be prepared by a process analogous to that used for active nitrogen.

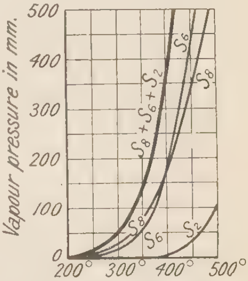
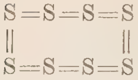
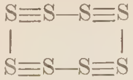


FIG. 17.—The Total and Partial Pressures of Sulphur in Different Molecular States.

The various methods for determining the **molecular weight** of sulphur show that, in all probability, this element, in the solid, liquid, or vaporous state (at a low temp.), has the complex molecule S_8. H. M. Vernon calculated S_2, for liquid sulphur at the b.p.; and W. Vaubel, $S_{11 \cdot 18}$. D. Pekar calculated S_8 from the surface energy of soln. of sulphur in carbon disulphide, and in sulphur monochloride; G. Guglielmo obtained S_8 from the vap. press. of dil. soln. of sulphur in carbon disulphide, and S_9, with conc. soln.; and J. N. Brönsted, from the heat of soln. of sulphur in benzene and choroform, obtained S_8. H. T. Barnes calculated $(S_4)_n$ from the sp. gr. of soln. of sulphur in carbon disulphide. The molecular complexity, calculated by A. M. Kellas from the molar surface energy, of λ-sulphur between 115° and 160°, approximates S_6; and at higher temp., it approximates to S_{18}. This agrees with the assumption that near 160° sulphur begins to polymerize to the complex S_{18} which remains stable up to the b.p.; and near 160°, $3S_6 \rightleftharpoons (S_6)_3$. Values calculated from P. Walden's, W. A. Kistiakowsky's, and P. Dutoit and P. Mojoiu's empirical relations agree with a complexity approximating S_6; from G. G. Longinescu's relation, S_{14}; and A. E. Dunstan and F. B. Thole's relation gives a still higher value. H. Erdmann, more or less arbitrarily, assumed that the μ-sulphur formed at about 160°, is S_3, the sulphur analogue of ozone, and he named it *thiozone*. He said that thiozone has the character of an acid anhydride, and is able to bring about the polymerization of eight-membered rings. Molten sulphur at 160° is therefore supposed to contain thiozone, which produces the dark colour, and amorphous $(S_8)_n$, which renders the mass viscid. He represented the molecules of the two different forms of crystalline sulphur graphically by the formulæ:



β-Sulphur.



α-Sulphur.

The former is supposed to represent monoclinic sulphur, and the latter rhombic sulphur. The experimental evidence upon which these formulæ are based is very flimsy. The subject was discussed by M. Copisaroff. The formula S_8 is in agreement with the observations of J. N. Hertz on the effect of sulphur on the f.p. of naphthalene; E. Kordes, naphthalene and iodine; of S. D. Gloss, of α-, β-, and plastic sulphur on naphthalene; and yellow phosphorus; A. Borgo and M. Amadori, bromoform; E. Beckmann, and R. Hanslain, with iodine, and anthraquinone; S. Tolloczko, antimony trichloride; and A. Smith and W. B. Holmes, and H. Biltz, of μ-sulphur on molten sulphur. E. Paterno and R. Nasini obtained S_6 with benzene soln.; and S. P. Popoff found that with α-, β-, and μ-sulphur in benzene, or dimethylaniline, the mol. wt. is proportional to the conc. E. Beckmann and P. Geib observed that with freezing bromine, sulphur mono-bromide is formed. F. Olivari, E. Beckmann and co-workers, and R. Hanslian measured the effect on the f.p. and b.p. of iodine, and obtained values corresponding with the mol. S_3. E. Beckman, J. Sakurai, and A. Helff calculated S_8 from the effect of sulphur on the b.p. of carbon disulphide; E. Beckmann, and R. Hanslian, diphenyl; L. Aronstein and S. H. Meihuizen used toluene, xylene, naphthalene, as well as carbon disulphide; G. Oddo and E. Serra, carbon tetrachloride; W. R. Orndorff and G. L. Terrasse obtained S_9 with carbon disulphide, and toluene; S_2 with sulphur monochloride; and S_8 with solvents having a b.p. above the m.p. of sulphur. G. Timoféeff obtained S_6 with chloroform, S_8 with carbon disulphide, and S_5 to S_{10} with benzene. E. Beckmann and P. Geib obtained S_2 with liquid chlorine, but probably sulphur monochloride was formed; with boiling sulphur monochloride, the complex sulphur molecules appears to be split into S_2 and even to atoms. In stannic chloride, or arsenic trichloride, α-, β-, amorphous, and plastic sulphur form S_8-molecules. R. Auerbach found the mol. wt. of sulphur $(32{\cdot}06)_n$ calculated from its effect on the f.p. of pyrosulphuric acid with 0·3117, 0·7775, and 1·2400 grms. of sulphur in 413·7 grms. of pyrosulphuric acid to be $n=2{\cdot}09$, 2·13, and 1·86 respectively. Hence, the sulphur is in the diatomic form. Analogous results were obtained with soln. of sulphur in pyrosulphuric acid containing some sulphur trioxide.

P. A. Daguin[7] found that the crystals of α-sulphur have a **hardness** of 1·5 to 2·5, on Moh's scale; F. R. Rydberg, and A. Reis and L. Zimmermann said 2. Rhombic sulphur is brittle, and crackles when warmed with the hand owing to the production of fine cracks. It is very friable after dipping in boiling water, but not so if slowly cooled. A. Breithaupt said that monoclinic, or β-sulphur, is rather harder than α-sulphur. The effect of heat on the **viscosity** of molten sulphur has been already indicated in a general way. The observations of J. B. A. Dumas,[8] C. M. Marx, M. L. Frankenheim, C. J. St. C. Deville, and G. Osann have shown in a general way that sulphur melts, forming a limpid liquid which begins to thicken near 160°, and becomes quite stiff at about 200°. G. Pisati said that the maximum in the viscosity curve is between 157° and 160°; J. Brunhes and J. Dussy, 156° to 157°; K. Schaum, at 155°; P. Mondain-Monval, 160°; A. Smith and W. B. Holmes, below 159·5°; G. Pisati, at about 195°; J. Brunhes and J. Dussy, at 162°; K. Schaum, between 168° and 250°; and A. Smith and W. B. Holmes, between 170° and 220°. C. Malus made some observations on the effect of temp. on viscosity. C. C. Farr and D. B. MacLeod found that the viscosity of twice-distilled, but not gas-free sulphur, is $\eta=0{\cdot}1094$ at 123°, and from this temp. falls to a minimum, $\eta=0{\cdot}0709$ at 150°; it then rises to 0·075 at 159°, but nothing of the nature of a strict transition point can be observed. Exposure to air in the molten condition, especially below 160°, has a marked effect on the viscosity above 160°. The effect is a slow one, the viscosity continuing to rise for as much as 48 hrs. on exposure to air for that time. The maximum for purified, gas-free sulphur is reached at 200° when $\eta=215$, while with purified sulphur, not gas-free, after a long exposure to air, the maximum is about $\eta=800$. Crystallization has an apparent, but probably secondary, effect on the viscosity. It raises the viscosity of a low-valued sample and lowers that of a high-valued one; and the effect disappears with a sample having $\eta=300$ at 171°. Sulphur freed from gaseous impurities acts as a simple substance so far as its viscosity is concerned, since it is definite at any given temp., and is independent of previous heat treatment. Sulphuric acid is the impurity which causes the variations in viscosity with sulphur which has been exposed to air. Changes in viscosity are accompanied by corresponding changes in the amount of insoluble sulphur present. The relation between the viscosity and the presence of allotropic forms of sulphur in the liquid has been discussed by M. L. Frankenheim, K. Schaum, F. Hoffmann and R. Rothe, A. Smith and W. B. Holmes, C. Malus, J. Dussy, G. Magnus and R. Weber, etc. L. Rotinjanz said that the changes of viscosity exhibited by liquid sulphur are not to be attributed to the presence of amorphous insoluble sulphur. When the temp. of sulphur is increased at the rate of 0·27° to 1·0° per minute, the maximum viscosity is 52,000 (water unity) at 187°; if the rate of heating has been greater, the maximum occurs at higher temp. With sulphur, the temp. of which has been lowered gradually, the maximum value of the viscosity and the temp. at which it occurs depend on the temp. to which the sulphur has been raised previously, *a*, *b*, *c*, Fig. 18, the higher the temp. to which the sulphur has been heated the lower is the maximum value of the viscosity, and the higher is the temp. at which it is found. Sulphur through which a current of ammonia has been passed has a maximum viscosity of 19,000 at 180°; sulphur containing 0·02 per cent. iodine has a maximum viscosity of 5600 at 225°, *d*, Fig. 18, whilst with a content of 0·77 per cent. iodine, the maximum viscosity is only 300 at 265°. The relation of the viscosity curve obtained with rising temp. to that obtained with falling temp. is very much the same for these samples of sulphur as for pure sulphur. In the case of sulphur which has been treated with ammonia, there is a break in the falling branch of the viscosity curve at 210°, marked also by a change of colour similar to what is observed in the case of pure sulphur at higher temp. L. Rotinjanz gave:

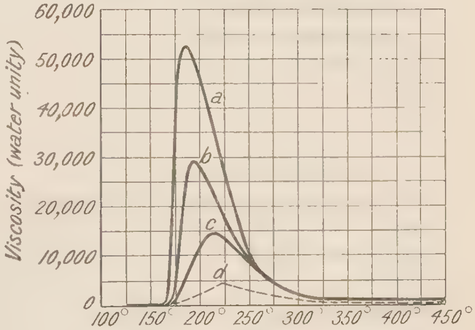


Fig. 18.—Viscosity Curves of Sulphur at Different Temperatures.

	120°	170°	187°	200°	240°	250°	300°	400°	448°
η .	11	30,000	52,000	46,000	24,000	9600	2200	150	74

The results are plotted in Fig. 18.

H. Zickendraht[9] measured the **surface tension** of molten sulphur, and found that from the m.p. up to 160°, the surface tension slowly decreases; at 160°, there is a maximum of about 6 mgrms. per mm., and thereafter a rise to a maximum at 250°, when the surface tension is about 12 mgrms. per mm. After the maximum there is a rapid fall in the surface tension to about 300°, and subsequently a gradual fall to the b.p. at which temp. the surface tension is about 4·5 mgrms. per mm. He explained the results by assuming that above 160°, a new allotropic form of sulphur appears in the system. Some observations on the ascent of the liquid in capillary tubes were made by G. Pisati, J. F. C. Schall, and R. Schiff. According to G. Capelle, there is a slight increase in the surface tension between 125° and 142°, and between 142° and 160°, a large and rapid increase; and at 160°, the liquid becomes too viscid to make observations by the method which he employed.

He also assumed that a variety of λ-sulphur, which he called *λ₁-sulphur*, exists between 125° and 142°, and another variety, *λ₂-sulphur*, between 142° and 160°, but the latter may be merely a mixture of λ_1- and μ-sulphur, such that the formation of the latter commences at 142° and is complete at 160°. W. A. D. Rudge found a change in the angle of contact between glass and drops of liquid sulphur at 185° and 256°, the observed angles being 60°, 43·4°, and 26·6° respectively at 130°, 190°, and 260°. He found the surface tension at 133° to be 11·56 dynes per cm. At higher temp. the surface tension is anomalous, but there is no sudden change at the temp. at which the angle of contact of liquid drops exhibits variations; but A. M. Kellas showed that this statement is based on an experimental error. W. A. D. Rudge said that the presence of mercury vapour changes the form of the drops of liquid sulphur and makes the sulphur adhere to the walls of the vessel. A. M. Kellas found for mobile or λ-sulphur between 119·4° and 156·04° the surface tension $\sigma=60{\cdot}46$ to 56·38 dynes per cm., and the mol. surface energy $\sigma(Mv)^{\frac{2}{3}}=653{\cdot}4$ to 615·9 ergs; at 116·4°, 132·0°, 142·8°, and 155·6°, $D=1{\cdot}807$, 1·795, 1·787, and 1·776 respectively; $\sigma=59{\cdot}48$, 57·72, 56·77, and 55·08 dynes per cm.; and $\sigma(Mv)^{\frac{2}{3}}=642{\cdot}4$, 626·1, 617·7, and 601·6 ergs respectively, whilst for viscous or μ-sulphur, he obtained:

	155·8°	183·5°	211·0°	241·0°	280·0°	302·0°	357·0°	445·0°
D	1·776	1·765	1·751	1·734	1·710	1·699	1·657	1·605
σ	55·82	54·69	52·83	50·51	48·55	47·31	44·27	39·87
$\sigma(Mv)^{\frac{2}{3}}$	609·6	599·2	582·0	560·6	544·1	532·1	506·5	466·0

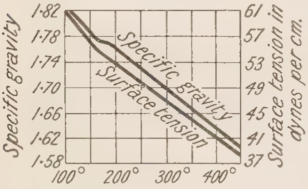


FIG. 19.—Specific Gravities and Surface Tensions of Liquid Sulphur at Different Temperatures.

The results are plotted in Fig. 19. A. M. Kellas gave for the **specific cohesion** of sulphur, $a^2=6{\cdot}8$ at 119·4°.

H. Rinde [10] measured the **osmotic pressure** of a colloidal soln. of sulphur in dil. hydrochloric acid separated by a collodion membrane from dil. hydrochloric acid; the membrane potential has its highest value when the acidity of the colloid is small, decreasing when the acidity rises, and finally approaches zero. The curve for osmotic press. against acidity has the same shape as the membrane potential curve, but approaches a certain positive value instead of zero. This should correspond with the osmotic press. of the colloid particles themselves, but the values are actually in the reverse order to that expected from an ultra-microscopic examination of the sols. All the calculated osmotic press. are many times larger than those observed. It thus appears impossible to calculate either the size of the particles or the membrane equilibrium from the osmotic press. The adsorption of the chlorine ions by the sulphur particles varies with the conc. of unadsorbed ions. L. Kahlenberg studied the selective dialysis of sulphur and sugar in pyridine soln. through a rubber membrane.

H. Rose and O. Mügge [11] found that the deformability or **plasticity** of rhombic sulphur are not appreciably increased by heating up to 281° at press. of 1000 to 19,600 kgrms. per sq. cm. T. W. Richards gave for the average **compressibility** of sulphur between 100 and 500 atm., 0·0000123 kgrm. per sq. cm.; 0·0000125 megabars; or 0·0000127 atm. E. Madelung and R. Fuchs gave $12{\cdot}56\times10^{-6}$ megabar per sq. cm. P. W. Bridgman gave for the compressibility of rhombic sulphur at a press. p kgrms. per sq. cm.:

p			2,000	4,000	6,000	8,000	10,000	12,000
$\frac{\delta l}{l_0}$	a	30°	0·0099	0·0180	0·0246	0·0304	0·0357	0·0412
		75°	0·0104	0·0190	0·0261	0·0323	0·0372	0·0427
	b	30°	0·0093	0·0165	0·0224	0·0277	0·0323	0·0370
		75°	0·0113	0·0201	0·0273	0·0334	0·0388	0·0433
	c	30°	0·0042	0·0079	0·0113	0·0143	0·0171	0·0198
		75°	0·0043	0·0082	0·0116	0·0148	0·0177	0·0203
$\frac{\delta v}{v_0}$		30°	0·0233	0·0419	0·0571	0·0707	0·0839	0·0949
		75°	0·0258	0·0466	0·0638	0·0784	0·0908	0·1027

J. D. Strong[12] studied the stress-strain curves of plastic sulphur. P. de Wolf and E. L. Larison gave for the **tensile strength** in lbs. per sq. in. of cement made from mixtures of fused sulphur and sand :

Sulphur . .	25	35	40	45	50	100 per cent.
Tensile strength	90	310	400	310	110	250

The coeff. of linear **thermal expansion** was found by H. Fizeau[13] to average 0·00006413 at 40° ; and $0·0_46748$ at 50°. J. Dewar gave $0·0_4384$ between −190° and 17° ; H. Kopp, $0·0_44567$ between 0° and 13° ; $0·0_4743$ between 13° and 15° ; $0·0_48633$ between 50° and 78° ; $0·0_32067$ between 78° and 97° ; and $0·0_2103$ between 97° and 100°. A. Schrauf gave for the linear expansion in the direction of the three crystal axes, $a=0·0_46698165$; $b=0·0_47803127$; and $c=0·0_41982486$ at 17·96°, and $0·0_471384$, $0·0_486039$, and $0·0_421441$ at 21·252°. The mean value at 17·96° is $0·0_4549593$; and $0·0_459621$ at 21·252°. W. Spring obtained for the coeff. of cubic expansion, β, and the vol., v, attained by unit vol. at 0° :

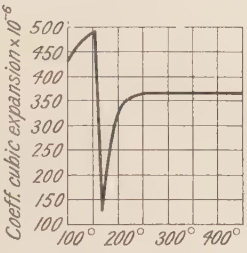


Fig. 20.—The Thermal Expansion of Liquid Sulphur.

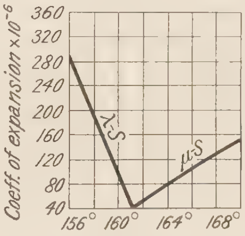


Fig. 21.—The Thermal Expansion of Viscid Sulphur.

		0°	20°	40°	60°	80°	100°
From	v .	1·000000	1·004243	1·009336	1·014632	1·023183	1·035408
CS_2 soln.	β .	—	$0·0_32122$	$0·0_32334$	$0·0_22438$	$0·0_32895$	$0·0_33541$
From	v .	1·0000000	1·0048616	0·10098893	1·0150350	1·0203378	1·0260503
Sicily	β .	—	$0·0_32430$	$0·0_32470$	$0·0_32500$	$0·0_32540$	$0·0_32600$

J. Russner found $\beta=0·0001723$ between 20° and 65° for α-sulphur which had been melted ; and for α-sulphur which had been crystallized from carbon disulphide, $0·0_3147$ at 10° ; $0·0_3160$ at 20° ; $0·0_3170$ at 30° ; $0·0_3178$ at 40° ; $0·0_3183$ at 50° ; and $0·0_3186$ at 60°. He gave for the vol., v, at θ°, for unit vol. at 0°, $v=1+0·0_3128\theta+0·0_5186\theta^2-0·0_7153\theta^3$. G. Vicentini and D. Omodei gave $\beta=0·0_3482$ at the m.p., 113° before melting, and $0·0_33540$ after melting. M. Töpler found for molten sulphur, 0·00041 between −20° and 0° ; 0·00043 between 0° and 20° ; 0·00046 between 20° and 40° ; and 0·00049 between 40° and 60°. Observations were made by C. Despretz, H. Kopp, G. Pisati, S. Scichilone, and A. Smith and W. B. Holmes. A. Moitessier found the coeff. of expansion of yellow, mobile sulphur, λ-S, decreases rapidly with rise of temp. from 110° to about 160°, and then, for brown, viscous sulphur, μ-S, rises rapidly beyond the minimum giving the V-shaped curve, Fig. 21. The following results by A. M. Kellas were calculated from the observed sp. gr., and refer to the mean coeff. between the indicated temp. and the next one :

	115°	134°	138·2°	145·5°	151·5°	156·9°	158·5°	161·0°
β . .	$0·0_3430$	$0·0_3439$	$0·0_3465$	$0·0_3487$	$0·0_3490$	$0·0_3282$	$0·0_3135$	$0·0_3127$
	165°	171·3°	178·3°	184·0°	210·0°	239·5°	278·5°	337°–445°
β . .	$0·0_3170$	$0·0_3194$	$0·0_3298$	$0·0_3308$	$0·0_3344$	$0·0_3366$	$0·0_3366$	$0·0_3366$

They are shown graphically, in part, in Fig. 21. F. C. H. Wiebe gave $\beta=0·0_32670$. Some relations between the m.p., b.p., and coeff. of expansion were studied by F. C. H. Wiebe, and P. Freuchen and V. Poulsen. A. Schrauf gave for the coeff.

of linear expansion of monoclinic, or β-sulphur at 21°, 0·0$_4$68486 for *a*, 0·0$_4$86039 for *b*, and 0·0$_4$21441 for *c*. These results are almost proportional to the ratios of the crystal axes. M. Töpler found for the coeff. of cubic expansion, β=0·00027 at 15°, and 0·00035 at 100°. M. Töpler also gave for insoluble, amorphous sulphur, β=0·0003 to 0·0004 at 30°.

L. Hecht[14] found the **thermal conductivity** of rhombic or α-sulphur to be 0·0017 cal. per cm. per sec. per degree of temp. G. W. C. Kaye and W. F. Higgins found for the thermal conductivity of rhombic sulphur:

	20°	40°	60°	80°	95° (transition)
k	0·00065	0·00061	0·00058	0·00055	0·00054

for monoclinic sulphur 0·00037 to 0·00040 at 100°; for plastic sulphur at 20°, *k*=0·0002; and for liquid sulphur, where the m.p. is 115°, and the change-point is between 160° and 170°:

	115°	120°	140°	160°	165°	170°	190°	210°
k .	0·00031	0·00031	0·00032	0·00033	0·00033	0·00034	0·00036	0·00037

H. V. Regnault found the **specific heat** of α-sulphur to be 0·1776 between 14° and 99°; P. L. Dulong and A. T. Petit, 0·1880; F. E. Neumann, 0·2090 for flowers of sulphur; and H. Kopp gave 0·163 between 17° and 45°; R. Bunsen, 0·172 between 0° and 100°; O. Silvestri, 0·1776; P. M. Monval, 0·176; F. C. H. Wiebe, 0·1710; L. Hecht, 0·187; A. Wigand, 0·1719 between 0° and 32°; and 0·1751 between 0° and 95°; F. Koref, 0·1537 between —77° and 50°; J. Dewar, 0·0109 between —253 and —196°; W. Nernst and co-workers, 0·1131 between —189·5° and —80·7°; 0·1537 between —76·9° and 0°; and 0·1705 between 1·7° and 46·5°; W. Nernst, 0·0300 at —250°, 0·0835 at —190°, and 0·1530 at —71°; H. Barschall, 0·118 between —183° and —73°; T. W. Richards and F. G. Jackson, 0·131 between —188° and 20°; and C. Forch and P. Nordmeyer, 0·135 between —192° and 14°. J. Heinrichs gave c=0·15702+0·0003436θ between 0° and 100°. W. A. Kurbatoff gave 0·1759 between 23° and 92°, and added that the at. ht. of sulphur at corresponding temp. is lower than those of the metals, indicating that the mol. of sulphur in the crystalline state is more complex than those of the metals. W. Herz discussed some relations of the sp. ht. The sp. ht. of monoclinic or β-sulphur is rather greater than that of rhombic sulphur. A. Wigand gave 0·1774 between 0° and 33°, and 0·1809 between 0° and 52°; W. Nernst and co-workers, 0·1187 between —189·0° and —80·1°; 0·1612 between —76·2° and 0°; and 0·1794 between 1·9° and 43·3°. W. Nernst found 0·0826 at —190°, 0·0920 at —182°, and 0·1498 at —72°. F. Koref gave 0·1612 between —76° and 0°. M. Padoa observed that the multiplication and intensification of bonds between atoms in solid polymerized compounds produces a marked decrease in the sp. ht., so that elements with sp. ht. lower than is required by Dulong and Petit's rule, should have a considerable number of valencies. When the abnormal elements form solid soln., the complex atom is resolved into a simpler atom; and hence the sp. ht. ought to rise with dilution. The S—Se-system agrees with this, for with solid soln. containing 4, 9, 28·77, and 90·35 per cent. of sulphur the at. hts. were respectively 7·03, 6·00, 5·50, and 5·78. C. C. Person obtained for liquid sulphur, 0·234 between 119° and 147°; and A. Classen, 0·232 between 116° and 136°. J. Dussy found the sp. ht. of molten sulphur to be 0·279 between 160° and 201°, 0·331 between 201° and 232·8°, and 0·324 between 232·8° and 264°. G. N. Lewis and M. Randall gave for the sp. ht. of liquid λ-sulphur c=0·21+0·00016θ; J. Heinrichs gave c=0·1546+0·00037θ between 112° and 210·5°. P. Mondain-Monval gave for liquid and vitreous sulphur respectively 0·220, and 0·290. For λ-sulphur with 3·1 to 5·5 per cent. of μ-sulphur they gave 0·238; for λ-sulphur with 5·5 to 23·7

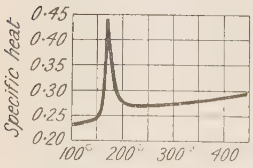


FIG. 22.—Specific Heat of Liquid Sulphur.

per cent. of μ-sulphur, 0·292; and for λ-sulphur with 23·7 to 33·9 per cent. of μ-sulphur, 0·263. The sp. ht. of liquid sulphur was represented by the curve in Fig. 22. I. Iitaka gave 0·199 for liquid sulphur at 119°. P. Mondain-Monval gave 0·176 for the sp. ht. of α-sulphur; 0·220, for liquid sulphur; and 0·290 for viscid sulphur above 160°.

From the above determinations, the **atomic heats** of α- and β-sulphur approach:

	−250°	−190°	−71°	0°	−190°	−182°	−72°	0°
At. ht. .	0·96	2·70	4·87	5·51	2·15	2·95	4·80	5·69
	α-sulphur.				β-sulphur.			

The estimated at. ht. from the summation law by H. Kopp is 5·52; by H. V. Regnault, 5·68; by M. Goldstein, 5·46; and H. Buff, 5·4 for bivalent sulphur, and 3·8 for sexivalent sulphur.

The early observations on the **melting point** of α-sulphur—104·5°, by J. J. Berzelius,[15] 107° by J. B. A. Dumas, 108°–109° by J. Dalton, 111° by G. Quincke, 111·75°–112° by R. F. Marchand and T. Scheerer, and 112·2° by M. L. Frankenheim—were too low. L. M. Arons, and G. Vicentini and D. Omodei gave 113°; G. Pisati, 113° to 113·5°; F. C. H. Wiebe, 113·6°; G. Tammann, 114·4°; B. C. Brodie, 114·5°; and C. C. Person, and H. Kopp, 115°. O. Silvestri found that crystals from a Sicilian mine had the m.p. 124°–125°, but this value is much too high. H. R. Kruyt, A. Smith and C. M. Carson gave 112·8° for the triple point of α-sulphur, liquid and vapour; and for the natural m.p. of α-sulphur with 3·5 per cent. of μ-sulphur, H. R. Kruyt gave 110·6°, and A. Smith and C. M. Carson, 110·2°. The **freezing point** of sulphur has been previously discussed, and it was shown by A. Smith and W. B. Holmes that the presence of a little μ-sulphur may lower the f.p. of λ-sulphur, which solidifies as α-sulphur. The equilibrium conditions are illustrated in Fig. 10, where 114·5° is taken as the natural m.p. of sulphur which is in equilibrium with 3·7 per cent. of μ-sulphur at that temp. By extrapolation it was found that the m.p. of idealized α-sulphur, freed from μ-sulphur, is 119·25°. W. Guertler and M. Pirani gave 119·2°. E. Beckmann and his fellow-workers' contribution to this subject has been discussed in connection with the allotropes of molten sulphur. The effect of press. is to raise the m.p.; thus, G. Tammann found the following m.p. at a press. of p kgrms. per sq. cm.:

p .	199	534	914	1318	1588	1838	2149	2650	3143
M.p.	120·01°	129·91°	141·1°	151·1°	158·1°	163·1°	170·1°	180·1°	190·1°

H. Rose and O. Mügge observed for p=19,300, the m.p. was 263°. W. Hopkins observed a m.p. of 135·2° at 519 atm., and 140·5° at 792 atm. The general effect of press. on the m.p. is illustrated by the line O_1O_2N, Fig. 6; the line O_1O_3 shows that α-sulphur is transformed into β-sulphur by press., as indicated previously. The m.p. of β-sulphur was found by K. Schaum to be 118·75°; by A. Wigand, 118·95°; and by A. Smith and W. B. Holmes, 119·25°. A. Smith and W. B. Holmes found that the m.p. was lowered 42·5° by the dissolution of 32 grms. of μ-sulphur in 100 grms. of β-sulphur. The natural m.p. of β-sulphur with 3·6 per cent. of μ-sulphur, was found by A. Smith and C. M. Carson to be 114·5°; by C. C. Farr and D. B. Macleod, 114·6°; and by H. R. Kryut, 114·6°. For γ-sulphur—that is, *soufre nacré*—A. Smith and C. M. Carson gave 106·8°—C. C. Farr and D. B. Macleod obtained a similar result—and for the natural m.p. of γ-sulphur, 103·4°; C. C. Farr and D. B. Macleod gave 103·2°. For ε-sulphur, or trigonal sulphur, R. Engel said that the m.p. is below 100°. For the variation in the m.p. owing to the association of molecules of different degrees of complexity, *vide supra*. A. Smith and W. B. Holmes found that the same liquid is produced by the melting of α- and β-sulphur. R. Lorenz and W. Herz studied some relations of the transition temp. and the m.p.; and W. Herz, and J. Meyer, the m.p., and the critical limits of existence of the liquid.

C. Brame,[16] and C. Zengelis observed that sulphur gives off vapour at ordinary temp. and blackens silver in its vicinity. J. Dewar also observed the sublimation of sulphur in an evacuated tube, at ordinary temp., when one limb of the tube is cooled by liquid air. M. Berthelot found evidence of the volatilization of sulphur in the drying chamber of a gunpowder works; J. Joly noted that sulphur volatilizes at 65° to 70°; and F. Jones found sulphur can be volatilized at 100°; and T. C. Porter, that it can be sublimed at 100° in vacuo. R. P. Tucker found that different varieties of sulphur sublime slowly at different temp. between 25° and 50°. Ordinary ground sulphur sublimes at 24° to 26°, sublimes sulphur at 30° to 35°, and gas purification sulphur at 40° to 45°, and the comparative rates were as 1 : 6 : 80. R. J. Moss observed that when some fragments of roll sulphur were left sealed up in an exhausted tube, after 25 years, a minute crystalline sublimate formed. A. Schrotter made an analogous observation. G. Aminoff found that with a sphere of rhombic sulphur, volatilization develops plane faces which correspond with the most important faces of the crystal.

According to M. Chavastelon, the **vapour pressure** of sulphur is appreciable at ordinary temp. because if small pieces of rhombic sulphur be kept in contact with or near to sheets of copper, silver, or lead, a circular film of sulphide forms on the metal around the sulphur. The result is affected by time, temp., and light. With dry air inside a tube within which was placed a quartz tube containing sulphur and wrapped round the outside with copper, silver, or lead wire, no tarnishing of the metal occurred at ordinary temp. and exposed to light for 19 months, but with moist air, a faint tarnishing occurred. O. Ruff and H. Graf found the vap. press., p, in mm. of mercury for sulphur between 49·7° and 211·3°:

	49·7°	78·3°	99·3°	104·0°	114·5°	123·8°	141·0°	172·0°	211·3°
p .	$0{\cdot}0_{3}34$	$0{\cdot}0_{2}23$	$0{\cdot}0_{2}89$	0·0115	0·0285	0·0535	0·131	0·629	3·14
	Solid.					Liquid.			

W. Matthies gave the following values for the vap. press. of liquid sulphur between 210·2° and 379·4°:

	222·4°	230·6°	241·8°	265·0°	306·5°	341·7°	352·5°	363·0°	379·4°
p .	3·2	4·48	8·45	20·5	53·5	105·5	133·0	176·0	250·1

M. Bodenstein measured the value of p between 374°, when $p=240$ mm., and 444·53°, when $p=760$ mm.; and E. F. Mueller and H. A. Burgess over the range 700 to 800 mm. H. V. Regnault gave the following values between 390° and 570°:

	390°	400°	440°	448·5°	480°	520°	540°	560°	570°
p .	272·31	328·98	663·11	760	1232·70	2133·30	2739·31	3465·33	3877·08

H. V. Regnault represented his results by the formula $\log p=5{\cdot}1545031-2{\cdot}7445700\alpha^{\theta\ {\cdot}387}$, where $\log \alpha=\bar{1}{\cdot}9986684$; while C. Antoine employed $\log p=2{\cdot}6150\{2{\cdot}7346-1000(\theta+164)^{-1}\}$; and C. Barus, $\log p=19{\cdot}776-4458\theta^{-1}-3{\cdot}868/\log \theta$. H. Grüner represented his measurements with α-sulphur, at θ°, between 50° and 100°, by $p=ab^{\theta}$, where $\log a=\bar{7}{\cdot}9225$, $\log b=0{\cdot}0395$; while for values of θ over 100°, $\log a=\bar{3}{\cdot}8725$, $\log b=0{\cdot}0316$, and in place of θ put θ—100. He found:

	50°	70°	80°	100°	100°	105°	110°	120°
p . . .	$0{\cdot}0_{4}8$	$0{\cdot}0_{3}47$	0·0012	0·0072	0·00745	0·0104	0·0136	0·0339
	α-sulphur.				β-sulphur.			

The observations of A. Smith and co-workers were made on fused sulphur containing definite proportions of λ and μ-sulphur. M. Volmer and I. Estermann found the fraction α of vaporized sulphur condensed on a cooled surface, while the rest (1—α) is reflected, lies between 0·2 and 0·5. R. Lorenz, and W. Herz studied some vap. press. regularities with sulphur and other elements. In connection with the vap. press. of sulphur, and Lord Kelvin's (*i.e.* W. Thomson's) formula for the vap. press. of small drops of liquid—**1.** 9, 6—W. Ostwald said:

The existence of such a difference can be demonstrated by putting a liquid which must not be too volatile, in a tube which is evacuated and sealed, and then producing a deposit of droplets on its walls. If the tube be put aside for some time, it will be found that droplets which were larger than the others at first have surrounded themselves with cleared spaces showing that the neighbouring small droplets have distilled over to the larger ones. Sulphur is a suitable material for this experiment.

S. L. Bigelow and H. M. Trimble showed that the clear zone cited by W. Ostwald is produced only when the central particle is solid. No distillation was observed to occur from the small droplets on to the large ones if the droplets be all kept in the liquid state.

The **boiling point** of sulphur at different press. corresponds with the saturation vap. press. at different temp. just indicated. J. B. A. Dumas[17] gave 440° at 760 mm.; H. V. Regnault, 448·4° at 760 mm.; J. W. Hittorf, 447° at 760 mm.; T. Carnelley and W. C. Williams, 446°–451°; V. Meyer, 444·4° at 724 mm., 435·6° at 760 mm.; A. L. Day and R. B. Sosman, 444·4° at 760 mm.; W. Ramsay, 446°; J. M. Crafts, 447·4°; H. M. Vernon, and H. le Chatelier, 448°; L. Holborn and F. Henning, 444·51°; C. T. Heycock and F. H. Neville, H. L. Callendar, W. Matthies, and H. L. Callendar and E. H. Griffiths, 444·53°; H. L. Callendar and H. Moss, 443·53°–443·55°; F. G. Keyes, 444·52°–444·54°; P. Chappuis, 444·6°; R. Rothe, 444·7°; N. Eumorfopoulos, 444·55°, and later 444·61°; E. Henning and J. Otto, 444·60°; P. Chappuis and J. A. Harker calculated for the b.p. at a press., p mm. of mercury, $360·498+0·1406539p-3443141\times10^{-5}p^{2}$, so that in proximity with the b.p., $dT'_b/dp=0·088°$ per mm. of mercury press. L. Holborn and F. Henning gave between 650 and 850 mm., $445·00°+0·0912(p-760)-0·000042(p-760)^2$; J. A. Harker and F. P. Sexton, $\theta_6+0·0904(p-760)-0·0_452(p-760)^2$, where θ_6 represents the b.p. at 760 mm.; and K. Scheel, $444·55+0·0908(p-760)-0·0_447(p-760)^2$. F. Krafft and L. Merz found that in the vacuum of the cathode light, sulphur boils at 140°, while at 40 and 115 mm., the temp. of the vapour of normally boiling sulphur is respectively 136°–138°, and 151°–152°; similarly at the same press., the temp. of the vapour of colloidal sulphur is respectively 183°–187°, and 199°–202°; while the temp. of the colloidal sulphur is respectively 204°–208°, and 223°–225°. The existence of colloidal sulphur is thus dependent on the press. W. Meissner, E. F. Mueller and H. A. Burgess, and C. W. Waidner and G. K. Burgess discussed the b.p. of sulphur as a fixed thermometric point. M. Delépine observed that the substitution of sulphur for oxygen in organic compounds usually raises the b.p., except in the case of water, and the lower alcohols, phenols, and acids. H. F. Wiebe studied the relation between the b.p., the m.p., the sp. ht., the coeff. of expansion, and the at. wt. of the family of elements; and K. Bennewitz, the vaporization coeff. M. Volmer and I. Estermann discussed what they called the coeff. of vaporization. According to E. F. Mueller and H. A. Burgess, the presence of 0·05 per cent. of arsenic in the sulphur has no effect on the b.p., but 0·10 per cent. raises the b.p. 0·02°; 0·05 per cent. of selenium, together with 0·10 per cent. of arsenic, raises the b.p. 0·08°, and 0·10 per cent. of arsenic and 0·10 per cent. of selenium raises the b.p. 0·09°. The b.p. of pure sulphur at 760 mm. press. is 421·73°, and the b.p. θ_b, at a press., p, between 700° and 800° is $\theta_b=444·60+0·0910(p-760)-0·000049(p-760)^2$. A. W. C. Menzies observed that the results are the same whether the b.p. is determined with fresh or with aged sulphur.

G. Tammann[18] gave 151° and 1320 kgrms. for the constants of the **triple point** of rhombic sulphur, and H. W. B. Roozeboom gave 131° and 400 atm. H. R. Kruyt studied the relations between the three triple points (Fig. 6) of sulphur. H. Rassow gave 1040° for the **critical temperature**; and A. M. Kellas calculated a critical temp. of 1390° for mols. of complexity S_{16}; and 766° for mols. of complexity S_6. The subject was discussed by F. Michaud, and E. van Aubel. C. C. Person found the **heat of fusion** of rhombic sulphur to be 0·300 Cal. per gram-atom or 9·37 cals. per gram at 115°; and for monoclinic sulphur, A. Wigand found 0·33 Cal. per gram-atom, or 10·4 cals. per gram; while P. M. Monval gave 9·3 cals.

per gram. K. Stratton and J. R. Partington gave 8·85 cals. per gram of monoclinic sulphur; J. Heinrichs, 9·855 cals. per gram; and G. N. Lewis and M. Randall, 14·9 cals. per gram for rhombic sulphur in a state of equilibrium at 100°, and 11·5 cals. per gram for monoclinic sulphur; the heat of fusion to form pure liquid λ-sulphur is 14·5 cals. for rhombic sulphur, and 11·1 cals. for monoclinic sulphur. I. Traube obtained 0·362 Cal. per gram for the **heat of vaporization** at 396° when the calculated value is 0·3399 Cal. C. C. Person gave 362 cals. per gram, or 11·58 Cals. per gram-atom. J. H. Awbery gave 79 Cals. per gram. F. S. Mortimer made observations on this subject. He calculated 16·92 Cals., and gave 15·670 for **Trouton's constant.** F. A. Henglein studied this subject. G. Preuner and I. Brockmöller calculated that the passage of 64 grms. of solid rhombic sulphur into gaseous S_2-mols. is accompanied by an absorption of 32,500 cals. G. Preuner and W. Schupp gave 28,800 cals., and they calculated that in the reaction $3S_8=4S_6$, 29,000 cals. are absorbed; in the reaction $S_6=3S_2$, 6400 cals. are absorbed; the change of gaseous S_8 to $4S_2$ absorbs 95,000 cals.; the heat of vaporization of solid 8S to gaseous S_8-mols., is 20,000 cals.; while for the conversion of 8S-solid to $4S_2$-gaseous mols., 115,000 cals. are absorbed. F. Pollitzer gave for the conversion of solid sulphur to S_2-mols., an absorption of 28,500 cals. N. Bjerrum tried unsuccessfully to calculate the heat of the reaction $S_2\rightleftharpoons2S$ at 2299° and 3404°, from the explosion of hydrogen sulphide with electrolytic gas in a calorimetric bomb. For the **heat of combustion** of rhombic or α-sulphur, P. L. Dulong gave (α-S, O_2) =83·2 Cals.; H. Hess, 82·2 Cals.; T. Andrews, 73·8 Cals.; P. A. Favre and J. T. Silbermann, 71·04–71·2 Cals.; M. Berthelot, 69·1 Cals.; T. Thomsen, and E. Petersen, 71·08 Cals. For monoclinic or β-sulphur, T. Thomsen, and E. Petersen gave 71·72 Cals.; and for insoluble, amorphous, or μ-sulphur, E. Petersen gave 71·99 Cals. H. Giran found for the heat of formation, Q Cals., of sulphur dioxide and the ratio, R, of sulphur converted into trioxide to the total weight of sulphur when that element is burned at a press. of p atm.:

p . .	1	2·5	5	15	20	25	35	45
Q . .	69·8	70·43	71·60	74·45	75·52	77·88	80·26	81·13
R . .	—	0·142	0·165	0·188	0·219	0·228	0·294	0·312

J. Thomsen compared the heats of combustion of numerous organic sulphur compounds; and W. Svientoslavsky concluded that the heat of formation of the linking C.S is greater in sulphides than in the corresponding mercaptans. A similar result was obtained with the corresponding ethers and alcohols. E. Mitscherlich observed that a rise of temp. occurs during the transformation of β- to α-sulphur, eq. to 2·27 units of heat. This is eq. to 0·063 Cal. at 15° in gram-atoms. T. Thomsen said that the **heat of transformation** is 0·64 Cal.; for the transformation of μ- into α-sulphur, L. T. Reicher calculated 0·081 Cal. at 95·6°; G. Tammann, 0·086 Cal.; J. N. Brönsted, 0·077 Cal. at 0°; and H. R. Kruyt, 0·105 Cal. at 96°. A. Wigand gave −7·180 Cals. per mol., S_8, for the heat of transition from the soluble to the insoluble form at 117·1° to 119·6° as compared with −6·0 Cals. at 126·3°; −5·39 Cals. at 131·0°; and −4·70 Cals. at 135·9°. E. Petersen gave 0·91 Cal. per gram-atom; and H. von Wartenberg, 0·72 Cal. M. Berthelot found for the heat of the transformation of amorphous insoluble into amorphous soluble sulphur, 0·086 Cal. per gram-atom; and A. Wigand for the conversion of amorphous soluble-sulphur into α-sulphur, 0·64 Cal. per gram-atom. P. Mondain-Monval found that the heating and cooling curves of molten sulphur show discontinuities at 162·8° and 157·7° respectively; the heat of transformation of rhombic to monoclinic sulphur is 2·7 cals., and of liquid to vitreous sulphur, 2·8 Cals. According to R. G. W. Norrish and E. K. Rideal, if C cals. denotes the critical increments of the reaction at 300°, and n, twice the number of free bonds of sulphur produced when the sulphur reacts, then for $\frac{1}{2}(2H_2+S_2)$ gaseous reaction $C=51{,}460$, $n=4$, and $C/n=12{,}865$; for H_2+S surface reaction, $C=25{,}750$, $n=2$, and $C/n=12{,}875$; for the dissociation of the gas from H. Budde's result, $\frac{1}{2}S_2=2S$, $C=50{,}000$, $n=4$, and

$C/n=12{,}500$; for liquid sulphur to S_2-gas, F. Pollitzer's result, $C=28{,}000$, $n=2$, and $C/n=14{,}000$; for the latent heat of liquid sulphur per gram-atom from C. C. Person's result, $C/n=11{,}600$; for the allotropic change of liquid sulphur, $C=25{,}750$, $n=2$, and $C/n=12{,}875$; for the reaction A of $S+O_2$, $C=25{,}750$, $n=2$, and $C/n=12{,}875$; and for the reaction B of $S+O_2$, $C=37{,}450$, $n=(3)$, and $C/n=12{,}480$. This shows that the critical increment of the reaction is a constant numerically equal to one-half the work required to create one free sulphur bond. The subject was discussed by A. M. Taylor and E. K. Rideal, M. Born and E. Bormann, M. Born and W. Gerlach, and J. Franck and P. Jordan. For the **heat of solution** of a gram-atom of sulphur in benzene, S. U. Pickering gave $-0\cdot690$ Cal.; in chloroform, $-0\cdot697$ Cal.; in carbon tetrachloride, $-0\cdot624$ Cal.; in carbon disulphide, $-0\cdot624$ Cal.; and in ether, $-1\cdot499$ Cals. A. Wigand found the heat of soln. of rhombic sulphur in carbon disulphide is $-12\cdot3$ cals.; and of soluble amorphous sulphur, $-1\cdot0$ Cal. per gram. P. Mondain-Monval found the heat of transformation for liquid to viscid sulphur at 160° is 2·8 cals. per gram; and the transition α- to β-sulphur absorbs 2·7 cals. per gram. G. N. Lewis and co-workers found that the **free energy** of formation of β-sulphur is 17·5 cals. when that of α-sulphur is zero; for liquid λ-sulphur, 94 cals.; and for equilibrium mixture of λ- and μ-sulphur, $-0\cdot8$ Cal. G. N. Lewis and co-workers gave 7·6 for the **entropy** of rhombic sulphur, and 7·8 for monoclinic sulphur; and B. Bruzs gave 9·6 at the m.p. W. Herz discussed the subject. W. C. McC. Lewis calculated that the **critical increment** of the energy which must be added to a molecule of sulphur, S_8, in excess of the average energy, in order to produce a S_2-molecule from the corresponding quantity of S_8-molecules is 147,000 cals.; or 735,000 cals. per gram-atom. E. Kordes calculated Q cals. $T=0\cdot775$ for S; 3·1 for S_4; 4·65 for S_6; and 6·2 for S_8. S. Pagliani found that the theoretical **temperature of combustion** of sulphur in the calculated proportion of air is 1616° at constant press., and 2000° at constant vol. K. Jellinek and A. Deubel calculated the **chemical constant,** 2·43, of sulphur vapour.

According to W. H. Wollaston,[19] the light refracting power of α-sulphur to that of water is 0·204 : 1·336. A. des Cloizeaux gave for the **indices of refraction** of Sicilian sulphur at 17°, $\beta=2\cdot023$ for red-lithium light, 2·043 for yellow-sodium light, and 2·082 for blue light. A. Schrauf gave $\alpha=1\cdot93651$, $\beta=2\cdot02098$, and $\gamma=2\cdot22145$ for the B-line; $\alpha=1\cdot95047$, $\beta=2\cdot03832$, and $\gamma=2\cdot24052$ for the D-line; $\alpha=1\cdot96425$, $\beta=2\cdot05443$, and $\gamma=2\cdot25875$ for the E-line; and $\alpha=2\cdot01704$, $\beta=2\cdot11721$, and $\gamma=2\cdot32967$ for the H-line. A. Cornu gave $\alpha=1\cdot958$, $\beta=2\cdot038$, and $\gamma=2\cdot240$ for Na-light; W. Schmidt, $\alpha=1\cdot9760$, $\beta=2\cdot0580$, and $\gamma=2\cdot2759$ for Tl-light; $\alpha=1\cdot9576$, $\beta=2\cdot0379$, and $\gamma=2\cdot2454$ for Na-light; and $\alpha=1\cdot9395$, $\beta=2\cdot0172$, and $\gamma=2\cdot2159$ for Li-light at 20°. L. M. Arons gave 2·080 for solid sulphur and 1·962 for molten sulphur with the D-line; and H. Becquerel gave 1·9290 at 114° for the D-line. For monoclinic β-sulphur, for Li-light, A. Schrauf gave $\alpha=2\cdot218503$ at 8°, 2·215780 at 20°, and 2·212930 at 30°; $\beta=2\cdot01937$ at 8°, 2·01709 at 20°, and 2·014160 at 30°; and $\gamma=1\cdot94157$ at 8°, 1·93975 at 20°, and 1·93770 at 30°. For Na-light, $\alpha=2\cdot248350$ at 8°, 2·245159 at 20°, and 2·242202 at 30°; $\beta=2\cdot040128$ at 8°, 2·037697 at 20°, and 2·02534 at 30°; and $\gamma=1\cdot959768$ at 8°, 1·957914 at 20°, and 1·955999 at 30°. For Tl-light, $\alpha=2\cdot278792$ at 8°, 2·275449 at 20°, and 2·272552 at 30°; $\beta=2\cdot061080$ at 8°, 2·058649 at 20°, and 2·056096 at 30°; and $\gamma=1\cdot978142$ at 8°, 1·976370 at 20°, and 1·974283 at 30°. E. Schmidt gave the results indicated in Fig. 23 for the indices of refraction of rhombic sulphur, and he found the constants in $\mu^2=m+m'\lambda/(\lambda^2-\lambda'^2)$ to be for the α-index $\lambda'=255\cdot49$, $m=2\cdot4292$, and $m'=1\cdot1392$; for the β-index,

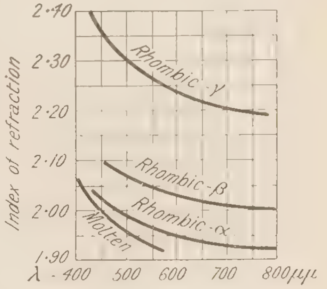


FIG. 23.—The Indices of Refraction of Rhombic and Molten Sulphur.

$\lambda'=208{\cdot}45$, $m=1{\cdot}5891$, and $m'=2{\cdot}2420$; and for the γ-index, $\lambda'=271{\cdot}68$, $m=2{\cdot}7580$, and $m'=1{\cdot}7987$. He also gave for molten sulphur, Fig. 23:

λ . .	399·5	408	425	441	468	480	508·5	537	568
μ . .	2·068	2·054	2·029	2·010	1·986	1·979	1·959	1·946	1·927

C. Cuthbertson and E. P. Metcalfe represented the refractivity of the vapour of sulphur by $\mu=1{\cdot}001046(1+2{\cdot}125\lambda^{-2}\times10^{-10})$. They said that the refractive index for infinitely long waves is, within 2 per cent., four times that of oxygen; the dispersions also are as 4 : 1. P. Mondain-Monval and P. Schneider observed a break at 160° in the index of refraction curve between 120° and 200°. V. Berghoff found the refractive index, μ, of g grms. of sulphur in 100 grms. of carbon disulphide at 15° to be:

g .	0	5	10	15	20	25
μ .	1·63172	1·64294	1·65294	1·66333	1·67232	1·68169

The index of refraction with soln. of different concentration changes almost the same with variations of temp. The sp. refraction, 0·4973 at 15° with the μ-formula and 0·280–0·276 at 25° with the μ^2-formula, is almost independent of the conc. and temp. of the soln. Observations were also made by C. Forch, and C. E. Guignet. H. G. Madan gave 1·778 for the refractive index of a sat. soln. of sulphur in methylene iodide at 16° with D-light; and G. Rossi and A. Manescotti, for soln. of colloidal sulphur in sulphuric acid. The **birefringence** of sulphur is high. G. Quincke measured the optical properties of sulphur cooled from the liquid state under different conditions. T. H. Havelock gave for the mol. refractivity of S'', 8·19. K. Spangenberg compared the mol. refraction of the oxides, sulphides, selenides, and tellurides; and W. Strecker and R. Spitaler, the relation between the index of refraction and the structure of organic sulphur compounds.

According to M. Delépine, in sulphur compounds, singly-linked sulphur has a mean at. refraction 7·84; except in the case of carbonyl joined to sulphur when the constant may be 9·26 as in $CS(OMe)_2$, or 9·68 as in $C_2H_5.CS.OEt$, and similarly constituted substances; and further variations occur as the compounds considered become more complex. In the case of sulphur singly-linked in nitrogen compounds, as in $C_2H_5.S.SN$, or $NEt_2.C(:NEt).SEt$, the mean at. refraction is about 8·00, but it shows considerable variation in the iminothiocarbonates and iminodithiocarbonates, and in the thiocarbamides becomes 10·75. In isomeric compounds containing sulphur similarly linked, the refractive indices are of about the same value, but an isomeride containing doubly linked sulphur always has a higher refractive index than one containing singly linked sulphur. The **atomic refraction** for H_α-ray, with sulphur, in its three states of aggregation, was found by R. Nasini and T. Costa to be 15·5 to 16·0 respectively with the μ-formula, and 7·7 to 8·2 with the μ^2-formula. With the μ-formula, E. Wiedemann found 14·04 for single-bonded sulphur, and 15·20–17·45 for double-bonded sulphur; while with the μ^2-formula, single-bonded sulphur gave 7·94, and double-bonded sulphur, 9·09–9·44. R. Nasini gave for single- and double-bonded sulphur, respectively, 14·10 and 15·61 with the μ-formula, and 7·87 and 9·02 with the μ^2-formula—using the H_α-line. According to J. H. Gladstone, the at. refraction in its three states of aggregation is 14 for single- and 16 for double-bonded sulphur. The at. dispersion is, respectively, 1·2 and 2·6. R. Nasini found for compounds of the type SX_2, where X denotes hydrogen, a halogen, an alkyl-radicle or a metal, the at. refraction is between 11·78 and 17·05 with the μ-formula, and between 7·52 and 8·51 with the μ^2-formula; if in compounds of the type SX_2, the sulphur is connected with a carbon atom which is in turn united with oxygen or nitrogen, the at. refractions by both formulæ are in agreement, and also with the results with SX_2 compounds. In polysulphides containing a $S-S$-group, in compounds of the type XS_nX, where X is a univalent metal or radicle, the at. refraction with both formulæ are nearly the same; the sulphur in compounds with the $S=C$-group, and the sulphur in sulphur dioxide and its oxy-derivatives has a high refraction and dispersion; while in sulphines of the type SX_4, the at. refraction has not a constant value. I. I. Kannonikoff found the at. refraction of bivalent sulphur is 14·1; quadrivalent sulphur, 8·72; and sexivalent sulphur, 4·85; while H. Hertlein obtained for bivalent sulphur, respectively with the μ- and μ^2-formulæ, at 20°, and Na-light, 14·44 and 8·46 for $K_2S_2O_6—K_3S_3O_6$; 14·70 and 8·53 for $K_2S_3O_6—K_2S_4O_6$; 15·53 and 9·02 for $K_2S_4O_6—K_2S_5O_6$; and 14·30 and 8·36 for $BaS_2O_6—BaS_4O_6$. Observations were also made by E. Ketteler, G. H. L. Hagen, J. A. Wasastjerna, A. Schrauf, R. Nasini and G. Carrara, and S. Opolsky. C. P. Smyth studied this subject; and J. E. Calthrop, the relation between the at. vol. and the index of refraction.

E. L. Nichols and B. W. Snow found the **reflecting power,** R, of molten sulphur for light of wave-length, λ, to be:

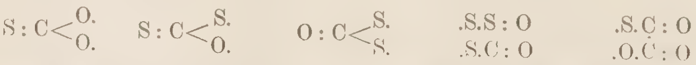
λ . .	6685	6080	5570	4920	4685	4500	4340
R 25° .	−0·682	0·651	0·634	0·571	0·318	0·163	0·055
R 103° .	−0·457	—	0·368	0·332	0·205	0·094	0·040

J. Kerr[20] found that the **electromagnetic rotation** of the plane of polarized light by sulphur is strongly positive, and H. Becquerel found that Verdel's constant for liquid sulphur at 114° with Na-light, is 0·0803. M. A. Schirmann, and G. I. Pokorowsky studied the polarization of light; B. Ray, and S. Venkateswaran, the scattering of light by sulphur suspensions; and Y. Björnstähl, the electric double refraction. J. C. McLennan and A. F. McLeod found that the Raman effect in liquid sulphur agrees with the assumption that weak di-poles $S^+—S^-$ are present. The subject was discussed by C. P. Snow.

The **flame spectrum** of sulphur or of hydrogen sulphide is continuous, but if a hydrogen flame contains only traces of sulphur, a band spectrum is produced. G. Salet[21] precipitated sulphur from the blue flame of burning sulphur by chilling the flame; W. R. E. Hodgkinson also said that a flame of moderate size will deposit sulphur on the cold surface of a substance placed in it, and hence he supposed that sulphur volatilizes before it burns, without considering if the sulphur came from the sulphur dioxide. W. D. Bancroft and H. B. Weiser showed that sulphur can be deposited from a hydrogen-sulphur dioxide flame. The band spectrum of sulphur was first observed by E. Mulder, by heating sulphur near the orifice of a glass tube from which there was a flame of hydrogen. G. Salet increased the luminosity of the flame by causing it to impinge on a stream of water falling vertically. G. Salet thought that this spectrum is the same as the spark spectrum in the vacuum-tube, but A. Schuster added that G. Salet's observations make it appear as a new spectrum where some of the lines may coincide with those obtained with the spark spectrum. Observations were made by W. F. Barrett, M. Faraday, R. Böttger, A. J. Angström, C. H. L. von Babo and J. Müller, A. Mitscherlich, J. J. Hopfield, H. C. Dibbits, K. Heumann, J. Salet, H. W. Vogel, W. H. Julius, W. N. Hartley, L. and E. Bloch, D. K. Bhattacharyya, P. Lacroute, and R. J. Strutt. If sulphur be heated in a vacuum tube, and the jar-discharge passed through the vapour, the **spark-spectrum** or the **line spectrum** appears, and the following lines are the most prominent: 5660, 6640, and 5605 in the yellowish-green; 5562, 5508, 5471, 5425, 5439, 5430, 5342, 5320, 5215, 5201, 5143, 5103, 5033, 5013, 4993, 4926, 4919, 4903, 4885, 4816, and 4716 in the green; and 4552, 4525, 4486, and 4464 in the indigo-blue region. This spectrum was first mapped by J. Plücker and J. W. Hittorf; and J. M. Séguin obtained it by passing a spark through the vapour of sulphur heated in hydrogen at atm. press.

If the ordinary discharge be passed through a vacuum tube, in which the sulphur is kept boiling, the so-called **band spectrum** is produced. This spectrum was observed by J. Plücker and J. W. Hittorf; and G. Salet first observed it as an absorption spectrum by passing the light through sulphur vapour at a high temp., and this was confirmed by D. Gernez, and J. N. Lockyer. J. I. Graham found that photographs obtained at constant press. over the above interval of temp. show that two distinct absorption spectra are present, and these are attributed to the molecular complexes S_8 and S_2, and that above 580° the S_8-molecules dissociate directly into the diatomic molecules, whereas at or below 520° dissociation takes place with the formation of molecules which are intermediate in complexity. The bands have a sharp limit in the violet and they shade off in the red. The more important bands are at 5366, 5221, 5191, 5089, 5041, 4991, and 4946 in the green; 4841, 4796, 4656, and 4616 in the blue; and 4471 in the indigo. Observations on the spark spectrum were made by J. Plücker, W. A. Miller, A. Mitscherlich, G. Salet, A. Ditte, A. J. Angström, R. Capron, B. Hasselberg, A. Wüllner, W. N. Hartley, E. Demarçay, J. Salet, A. de Gramont, E. Rancken, J. M. Eder and E. Valenta, P. G. Nutting, A. Hagenbach and H. Konen, E. Real, E. Goldstein, G. Stead, and F. Exner and E. Haschek. M. Curie studied the spark spectrum of liquid sulphur. The effect of *pressure* and *temperature* was studied by J. Evershed, and G. L. Ciamician; the effect of a *magnetic field*—the Zeeman effect—was examined by E. van Aubel, and G. Berndt; the effect of *self-induction*, by A. de Gramont; and the effect on the spectrum of argon, by R. C. Johnson and W. H. B. Cameron, and J. C. McLennan and co-workers. The **arc spectrum** was studied by A. L. Foley, and J. J. Hopfield. The spectrum of sulphur excited by activated nitrogen was examined by R. J. Strutt; of the cathode luminescence, by P. Lewis; and of the electrodeless discharge, by G. Balasse, and W. W. Shaver.

The continuous **absorption spectrum** of sulphur was examined by D. Brewster. It is seen when sulphur is heated in a 30-cm. tube closed so that a beam of light can be sent longitudinally through the vapour. D. Gernez showed that change of the continuous to the band spectrum seems to be connected with and dependent on the change in the vapour density of sulphur between 500° and 1000°. J. J. Dobbie and J. J. Fox found that the absorption spectrum shortens as the temp. is raised to 650°, after which it lengthens again; there is, therefore, a maximum absorption at this temp. which corresponds with the presence of S_3-molecules. They conclude, therefore, that at suitable temp., sulphur vapour contains S_2, S_3, and S_8 mols. M. Fukuda found that the absorption spectrum with a layer of sulphur 0·3 mm. thick, slowly heated until melted, extends from the ultra-violet up to $\lambda = 0{\cdot}408\mu$ at 0°, and extends a further $2\mu\mu$ towards the red end for every 10° rise of temp. up to 300°. No discontinuity was observed at about 160°. The absorption spectrum of plastic sulphur depends on the initial temp. to which the sulphur is heated during its preparation. The higher this temp., the further does the absorption extend from the ultra-violet towards the red end. The absorption spectrum was examined by G. Salet, J. Salet, J. N. Lockyer, W. Friederichs, G. D. Liveing and J. Dewar, J. Tyndall, T. P. Dale, P. Baccei, H. Deslandres, B. Rosen, A. M. Taylor and E. K. Rideal, M. C. Teves, V. Henri and M. C. Teves, E. Paterno and A. Mazzucchelli, W. W. Coblentz, V. Henri, R. Wildt, F. Lowater, and J. I. Graham—*vide infra*, sulphur dioxide. In agreement with J. I. Graham, R. G. W. Norrish and E. K. Rideal observed a band of maximum absorption in sulphur vapour at 2750 A. J. C. McLennan and co-workers studied the fluoresence spectrum of sulphur vapour. M. Fukuda found that the absorption of light by plastic sulphur is determined not only by the temp., but also by the temp. at which the plastic sulphur was prepared—the higher the initial temp., the longer the wave-length of the edge of the absorption band. He inferred that plastic sulphur is a complex mixture of S_6 and S_{18}-mols. J. E. Purvis and co-workers studied the absorption spectra of organic compounds in which sulphur replaced oxygen, and found that definite absorption bands are shown by sulphur compounds with the following structural groups:



$$S:C<\begin{matrix}O.\\O.\end{matrix} \qquad S:C<\begin{matrix}S.\\O.\end{matrix} \qquad O:C<\begin{matrix}S.\\S.\end{matrix} \qquad \begin{matrix}.S.S:O\\.S.C:O\end{matrix} \qquad \begin{matrix}.S.C:O\\.O.C:O\end{matrix}$$

but not when the sulphur is replaced by oxygen. The bivalent S : C-group is a powerful chromophore. In certain aromatic compounds—*e.g.* phenol, and benzyl alcohol—the replacement of oxygen by sulphur obliterates absorption bands.

Although oxalyl chloride is colourless, it gives yellow soln. with a number of unsaturated compounds, and compounds containing oxygen or sulphur. The **resonance spectrum** was studied by B. Rosen, who gave $\nu = a - 724{\cdot}5n - 2{\cdot}91n^2$, where a is 33,359 for the exciting mercury line 3132 A. The **ultra-red spectrum** was studied by W. H. Julius, A. M. Taylor, A. M. Taylor and E. K. Rideal, J. W. Ellis, V. J. Sihvonen, and W. W. Coblentz; and the ultra-violet spectrum, by J. L. Soret, J. J. Hopfield and G. H. Dieke, J. Gilles, P. Lacroute, E. L. Nichols, J. Pauer, J. M. Eder and E. Valenta, and G. Berndt. W. W. Coblentz found the percentage transmission or the selective absorption in the ultra-red of a plate of sulphur 3·6 mm. thick to be that indicated in Fig. 24. N. Pihlblad, and R. Audubert studied the absorption in alcoholic soln. of sulphur. G. T. Gibson, H. Graham, and J. Reid studied the effect of the valency and mode of linking on the absorption spectrum of sulphur. The **series spectrum**, or compound line spectrum of sulphur, has been observed only with spectra in spectrum-tubes. Nearly all the lines are included in a system of triplets similar to those with oxygen. This subject has been discussed by G. Salet, G. L. Ciamician, J. C. McLennan and co-workers, C. Runge and F. Paschen, I. S. Bowen, I. S. Bowen and R. A. Millikan, R. B. Lindsay, A. Schuster, J. J. Hopfield, O. Laporte, J. J. Hopfield and R. T. Birge, J. J. Hopfield and G. H. Dieke, E. Bungartz, B. Dunz, J. Gilles, A. Fowler, S. B. Ingram, D. K. Bhattacharyya, L. and E. Bloch, H. A. Kramers, and W. M. Hicks. G. Balasse discussed the continuous emission spectrum from the electrodeless discharge.

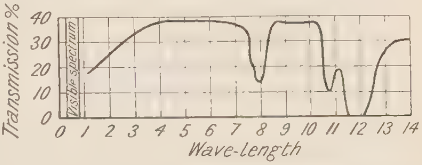


FIG. 24.—Ultra-red Transmission Spectrum of Sulphur.

H. Fricke and O. Glasser discussed the **ionization** of sulphur. M. Born and E. Bormann gave 2·16 volts for the **ionization potential,** and 50 units for the electron affinity of sulphur; while J. J. Hopfield gave 6·50 volts and 10·31 volts for the ionizing potentials of sulphur vapour; S. B. Ingram, 23·3 volts for the S-II-ion; B. Davis, 12·2 and 35 volts; and F. L. Mohler and P. D. Foote, 4·78 volts for the resonance potential and 12·2 volts for the ionization potential. F. Holweck obtained 163 volts for the critical potential of the L- and L_{111}-levels in the sulphur atom. G. Piccardi, and B. Rosen discussed this subject; R. N. Ghosh discussed the relation between the ionizing potential and the electronic structure, and S. C. Biswas, the mol. vol.

The K-series in the **X-ray spectrum** was found by H. Fricke,[22] O. Stelling, K. Chamberlain, P. A. Ross, H. Robinson, B. Ray, F. L. Mohler and P. D. Foote, D. M. Bose, Y. H. Woo, S. Aoyama and co-workers, A. Björkson, B. C. Mukherjee and B. B. Ray, W. Bothe, E. Bäcklin, A. E. Lindh and co-workers, B. Davis, L. A. Turner, and E. Hjalmar to include $\alpha_2\alpha'$, 5·36375; $\alpha_1\alpha$, 5·36090; α_3, 5·32837; α_4, 5·32174; $\beta_1\beta$, 5·0213; and $\beta_2\gamma$, 5·0128. S. K. Allison, F. Holweck, B.C. Mukherjee and B. B. Ray, and S. J. M. Allen studied the L-absorption spectrum; H. Duvallier observed no L_a-series with sulphur. C. G. Barkla studied the J-series; and B. C. Mukherjee and B. B. Ray, the M-series. E. Bäcklin compared the K-series in the X-ray spectrum of sulphur and barium sulphate, and inferred that the effect of the combination of an atom with other atoms is to displace the K-level nearer to the nucleus, and to displace the K-spectral lines towards shorter wave-lengths. C. Doelter found that thin layers of sulphur are not transparent to **X-rays**. L. M. Alexander, and B. B. Ray and P. C. Mahanti discussed the absorption of X-rays. G. L. Clark and co-workers studied the secondary and tertiary rays from sulphur exposed to X-rays. C. M. Slack studied the refraction of the X-rays; S. J. M. Allen, G. Schanz, T. E. Aurén, S. Aoyama and co-workers, and N. Ahmad, the absorption of X-rays by sulphur. K. Chamberlain found that in the absence of free oxygen, sulphurous acid is oxidized by exposure to the X-rays. L. Frischauer found that undercooled liquid sulphur crystallizes when exposed to **radium rays**. X-rays, and γ-rays are without influence; α-rays could not penetrate the glass of the containing vessel, hence the crystallization was induced by the **β-rays.** A. L. Foley examined the effect of exposure to X-rays, or to ultra-violet light on the spectrum of sulphur. Y. H. Woo measured the Compton effect with X-rays from sulphur as radiator. J. Stark and R. Künzer[23] showed that the **canal ray spectrum** of sulphur has an arc spectrum (series spectrum) which is attributed to positively charged molecules, S_2, carrying a single charge; the lines of a second arc spectrum are attributed to positive univalent sulphur atoms; the sharp spark lines are attributed to positive bivalent sulphur atoms; and the diffuse spark lines to positive tervalent sulphur atoms. M. Ishino and B. Arakatsu found that when carbon disulphide or sulphur dioxide is introduced into a positive ray tube, negatively charged sulphur atoms are formed. A. L. Hughes and A. A. Dixon gave 8·3 volts for the ionizing potential; and K. T. Compton, 4·25 volts. B. Davis studied the relation between the critical potential and the index of refraction. J. E. P. Wagstaff gave $7{\cdot}3 \times 10^{12}$ for the **vibration frequency** of sulphur; and W. Herz, $3{\cdot}88 \times 10^{12}$. F. Holweck, and W. Herz studied the vibration frequency of the sulphates; and M. Born and E. Bormann, the electro-affinity of sulphur.

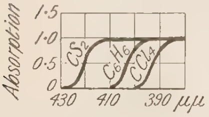


Fig. 25.—Absorption of Light by Solutions of Sulphur.

According to R. Audubert,[24] in the case of sulphur suspensions, very small granules are formed instantly on diluting the alcoholic soln. with water. These grains gradually grow both by fixing new molecules of sulphur and by agglomerating. **Light** of short wave-length accelerates this growth, but light of long wave-length inhibits it. There is an intermediate region in the yellow, which is without effect. The active radiations are most strongly absorbed by the suspensions. This growth of granule is a phenomenon similar to adsorption. Light modifies the speed of adsorption of the ions which constitute the "ionic environment" or "ionic atmosphere" of the granules. According to A. Lallemand, when a beam of light from the sun is directed through a sat. soln. of sulphur in carbon disulphide, amorphous sulphur is precipitated as a fine powder in the track of the ray of light. All the light from *A* to *G* is transmitted, while the violet, and ultra-violet light beyond *G* is absorbed. M. Berthelot verified these observations with light from the electric arc rich in ultra-violet rays. A. Wigand's measurements of the absorption of light by soln. of 36 grms. of sulphur in 100 c.c. of carbon disulphide; of 1·17 grms. of sulphur in 100 c.c. of benzene; and 1·1 grms. of sulphur in 100 c.c. of carbon tetrachloride, are illustrated by Fig. 25. M. Berthelot found that the heat of transformation is so small as to make it probable that light simply acts as an exciting agent and does not effect the work of transformation. E. Petersen observed an evolution of 910 cals., but the two varieties of sulphur may not have been the same. A. Wigand found that when a gram of insoluble sulphur is precipitated from a carbon disulphide soln., 15·8 cals. are absorbed, and rather less with soln. in carbon tetrachloride, or benzene. About 0·24 per cent. of the energy absorbed by the soln. from light is spent in bringing about the transformation. G. A. Rankin showed that, at a constant temp., the greater the conc. of the soln. of sulphur in carbon disulphide, the less the intensity of light for precipitation; and for light of a given intensity, the precipitation increases with rise of temp. Amorphous sulphur is likewise precipitated from soln. of sulphur in carbon tetrachloride, acetone, toluene, and benzene. M. Berthelot assumed that light acted only on dissolved sulphur, but G. A. Rankin showed that the reaction takes place more quickly in the case of the solvent because no surface film is formed. The result is a displacement of equilibrium between two solid phases: $S_{\text{rhombic}}\ (\text{dark}) \rightleftharpoons S_{\text{amorphous}}\ (\text{light})$. The reaction is reversible; the conversion of amorphous to rhombic sulphur takes place only in darkness or in very feeble light. Rhombic sulphur is the stable form in darkness; and amorphous sulphur, in light. Ammonia and hydrogen sulphide accelerate the reverse action—rhombic to amorphous sulphur—and prevent the precipitation of amorphous sulphur in sunlight. This is in agreement with the observations of A. Smith, and M. Berthelot. At 22·5°, with an arc-light, G. A. Rankin found that with light of varying intensity and soln. of sulphur in 100 grms. of carbon disulphide :

Candle-power . .	5	6·4	10·4	11·0	12·2	23·2
Grams sulphur . .	46·7	15·0	11·2	8·0	4·8	3·0

The results are plotted in Fig. 26. The curve *AB* represents amorphous sulphur in equilibrium with soln. and vapour ; the line *BC* represents the solubility curve of rhombic sulphur on the assumption that it is not affected by light. At *B*, rhombic sulphur, amorphous sulphur, solution and vapour, are in dynamic equilibrium. In the field above the curve, amorphous sulphur is the stable form, while below the curve, rhombic sulphur is the stable form. The light necessary to maintain amorphous sulphur in equilibrium with the soln. increases as the conc. decreases, until finally the curve approaches the line of ordinates asymptotically as the conc. approaches zero. As the conc. increases, the light necessary for equilibrium decreases until the point is reached at which, for a given temp., the solvent is sat. with respect to both forms of sulphur. This quadruple point for a temp. of 22·5° is not at the point of total darkness but at an intensity of about 5 candle-power. As the temp. for any given conc. is increased, the intensity of light required for equilibrium increases rapidly, showing that the rate of change of the amorphous sulphur increases with a rise of temp. At 40°, it takes about 45 candle-power to produce the first precipitation of amorphous sulphur from a sat. soln. A. Wigand found that the equilibrium $S_{soluble}$ (dark)$\rightleftharpoons S_{insoluble}$ (light) is displaced by light in favour of the soluble form ; and, as indicated above, the reaction is reversible.

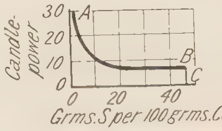


FIG. 26. — Equilibrium Curve of Amorphous Sulphur, Solution, and Vapour.

F. A. C. Gren,[25] S. F. Hermbstadt, and J. J. Berzelius observed that sulphur under certain conditions may exhibit a glow or **phosphoresence.** R. Robl observed no fluorescence in ultra-violet light. K. Heumann found that the glow is best obtained by placing sulphur on a shallow tray supported above the bottom of an air-bath at about 240°, and allowing a current of air to pass over the molten sulphur. When the conditions are properly regulated, a large flame is obtained, which differs from the usual blue flame of burning sulphur, and which is relatively cold. The cold flame can be maintained for a considerable time. The experiments of K. Heumann, E. Mulder, C. L. H. Schwarz, L. Bloch, O. Jacobsen, H. Moissan, and L. Bloch, and T. E. Thorpe show that phosphorescence begins at about 200° ; and of J. Joubert, 100°. W. H. Watson's observations lend no support to the view that a lower oxide of sulphur is formed during the glowing of the sulphur ; he concluded that when air passes over sulphur heated to a temp. below its ignition-point, the air becomes charged with sulphur vapour, which, as the temp. falls, separates as a mist or cloud of very small particles. The oxidation of this finely-divided sulphur gives rise to the phenomenon of the glow or phosphorescence, but there is no evidence that at any stage any oxide other than sulphur dioxide is formed. K. Heumann compared the smell which accompanied the oxidation to that of ozone or camphor. According to J. Joubert, the phenomenon is quite analogous with that of phosphorus ; oxygen is necessary, and there are upper and lower limits as with phosphorus, but L. Bloch showed that, unlike the case of phosphorus, the formation of ozone is not accompanied by any ionization phenomena. The combustion flame, which replaces the phosphorescence effect when the temp. of sulphur is raised to 360°, is non-conducting, and the oxidation of sulphur dioxide by air in contact with spongy platinum is also unaccompanied by the production of ions. H. J. Emeléus found that sulphur dioxide and a small proportion of the trioxide are the products of the phosphorescent combustion of sulphur. No traces of an oxide more volatile than the dioxide, and no evidence of the formation of ozone were observed. Sulphur shows no glow press. above which the oxidation is non-luminous. Sulphur dioxide, and a series of organic vapours inhibit the glow. The temp. at which the glow appears is higher, the greater the conc. of the inhibitant. H. B. Baker and R. J. Strutt observed a blue phosphorescence when ozonized oxygen is passed over sulphur. The **triboluminescence** of sulphur was not observed by J. P. Dessaignes, J. B. Beccari, and P. Heinrich; but E. Becquerel, and J. Bernoulli did observe the phenomenon.

F. Diestelmeier,[26] and W. Steubing found that, like oxygen, the vapour of sulphur exhibits a **fluorescence** at about 400°–500°, when exposed to the influence of white light, or the light emitted by the arc formed between electrodes of various metals; and when spark discharges are used as the source of excitation. The fluorescence is observed only with vapours of low density. J. O. Perrine found that sulphur showed no fluorescence on exposure to ultra-violet rays, or when exposed for 10 hrs. to X-rays. The wave-length of the light is between 2500 A. and 3200 A. The **fluorescence spectrum** is discontinuous, and shows more or less feeble groups of lines or bands. The fluorescence is greatly weakened by admixture with other gases or vapours. B. Rosen, and J. C. McLennan and co-workers studied this subject. F. Diestelmeier assumed that the centres of emission are diatomic molecules. F. Ehrenhaft observed a **photophoresis** with the particles of sulphur, for they move in a direction opposite to that of a beam of light—negative photophoresis. I. Parankiewicz showed that with particles of radius 8×10^{-6} to 60×10^{-6} cm., the sulphur particles are negative, and there is a maximum effect with particles 27×10^{-6} cm. The effect is independent of the press. and chemical nature of the surrounding gas. It is supposed that the effect is due to the direct action of light on the material—*cf.* selenium.

J. Monckman,[27] F. Kämpf, and A. Goldmann and S. Kalandyk found that sulphur exhibits a **photoelectric effect.** When light is absorbed by a photoelectrically active substance, in a thick enough layer, the photoelectrons are released in the substance itself as well as from the surface. If the substance is not a good conductor, as in the case of sulphur, the photoelectrons which do not emerge should impart a slight electrical conductivity during illumination. The temporary supply of free electrons accounts for the conductivity—*vide* selenium. The effect with sulphur requires light of wave-lengths shorter than about $\lambda=3300$ for its production. The subject was studied by M. J. Kelly. B. Kurrelmeyer showed that the current produced in sulphur by a given illumination, other conditions being equal, is directly proportional to the *applied electric field* from 20 to 15,000 volts per cm., as illustrated in Fig. 27. This is true for light of all intensities examined with the diamond, and zincblende. The curves depart from linearity with electric fields below those required for saturation. This means that if there is a saturation field for sulphur, it is above 50,000 volts per cm. No evidence of a secondary current could be detected with sulphur. The amount of excitation is the same whether it be pro-

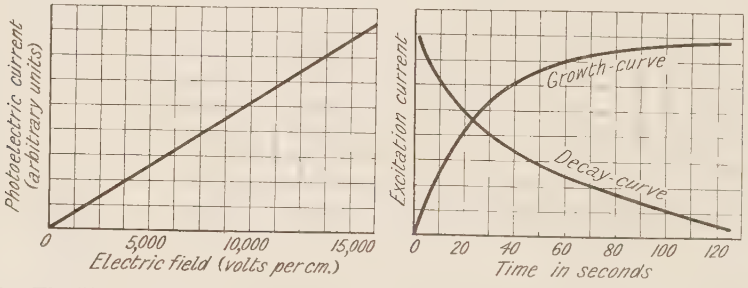


FIG. 27.—The Variation of the Photoelectric Current of Sulphur with the Strength of the Applied Electric Field.

duced with or without the field. The maximum value with illumination represents a state of equilibrium between the rate of formation of electrons, and their rate of recombination. The similarity of the growth and decay curves, Fig. 27, shows that the rate of recombination of the electrons is not influenced by the illumination. The variations of the photoelectric current are proportional to the *intensity of illumination*. The current reaches its full value in a very short time after the crystal has been illuminated, as shown in Fig. 28. As soon as the current flows, some of the positive ions begin to accumulate in the crystal, and these gradually reduce the effective field so that the current decreases with time during the illumination. *A*, Fig. 28, is the sum of the time photoelectric current, and the excitation current, and *B*, Fig. 28, represents the time photoelectric current. The curve representing the variation of the current referred to unit incident energy, and the wave-length of the incident light, *A*, Fig. 28, has a maximum at $470m\mu$, Fig. 29, and drops more slowly towards the red than towards the violet. The curve *B*, Fig. 29, represents the variation of the current referred to absorbed energy. There is a difference in connection with the *orientations of the crystal*. Currents in different directions in the crystal are equal in magnitude, but there is a unipolarity in the direction of the acute bisectrix of the optic axes with components in other directions. The reverse currents exhibit parallel differences. According to K. Scharf, the cloud of sulphur particles produced by condensing the vapour in nitrogen exhibits the normal photoelectric effect. L. Grebe found that sulphur becomes a better electrical conductor when exposed to the X-rays.

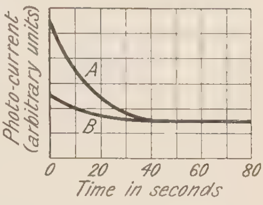


Fig. 28.—The Variation of the Photoelectric Current with Time.

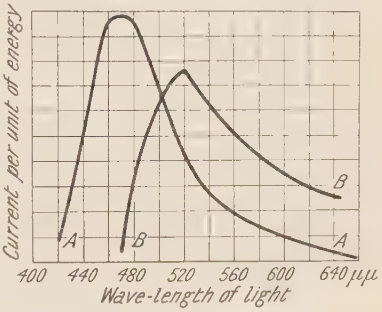


Fig. 29.—The Variation of the Photoelectric Current and the Wave-length of the Incident Light.

M. Faraday,[28] P. E. Shaw, P. Böning, and N. A. Hesehus and A. N. Georgiewsky found that lump sulphur is negatively electrified when rubbed against wood, or any of the metals tried, and electrifies them positively; yet M. Faraday found that a jet of air carrying powdered sulphur—flowers of sulphur—electrifies negatively both metal and wood, and even a sulphur cone; and when sulphur is held in a jet of steam it is negatively electrified, but air alone does not electrify the sulphur. H. F. Vieweg, and P. E. Shaw and C. S. Jex studied the frictional electricity of sulphur. According to W. E. Gibbs, the aerosol of sulphur—*i.e.* sulphur dust suspended in air—acquires a positive charge.

G. J. Knox stated that sulphur is a conductor of electricity, but M. Faraday could not confirm this. J. Monckman, and E. Duter also said that sulphur is a non-conductor at all temp. below its b.p., but at this temp. it is possible to pass an appreciable current through the liquid. A. Günther-Schulze, and K. F. Herzfeld discussed the metallic conductivity of sulphur. J. Monckman found that the sp. **electrical resistance** of precipitated sulphur at 440° is 5×10^5 ohms; and at 260°, 5×10^8 ohms; roll sulphur, 5×10^8 ohms at 125°, and $1·6\times10^5$ at 440°. For crystallized sulphur, R. Threlfall and co-workers observed at 75° that the resistance was $6·8\times10^{25}$ C.G.S. units. The resistance decreases to a marked degree as the temp. rises. Both soluble and insoluble sulphur are non-conductors; the conductivity at an elevated temp. is electrolytic, breaking up a combination of the two allotropes of liquid sulphur. The sp. resistance is 10^{28} C.G.S. units at ordinary temp. The presence of 5 per cent. of insoluble sulphur decreases the resistance, so that at ordinary temp. this falls to 10^{25} C.G.S. units. H. Neumann found at ordinary temp. that the resistance of sulphur is between 2×10^{18} and 2×10^{19} ohms. D. H. Black found that the conductivity of liquid sulphur increases to a maximum as the temp. rises from 130° to 160°; it then falls to a minimum at about 185°; and thereafter increases. This behaviour corresponds with the viscosity changes. The sp. resistance at 163° is about $7{\cdot}5\times10^{10}$ ohms. The conductivity is electrolytic in nature. S. Bidwell said that the conductivity of molten sulphur is really due to the formation of a sulphide by contact with the metal electrodes. The conductivity is favoured by exposure to light, possibly by the increased tendency to form sulphides in light. T. W. Case said that the poor electrical conductivity of sulphur is not appreciably affected by light; and J. Monckman observed an increased conductivity between graphite electrodes when the sulphur was illuminated, but R. Threlfall and co-workers could not confirm this. A. Wigand, also, was unable to detect any effect with light, and hence concluded that the electrical conductivity of the soluble and insoluble forms of sulphur are the same. According to M. Pigulewsky, the conductivity of amorphous sulphur is increased by light, but not so with crystalline sulphur. The maximum effect is obtained with rays of shorter wave-length than $280\mu\mu$. He found that the conductivity of crystalline sulphur increases with rise of temp. to a maximum at about 140°–150°, and afterwards continues to fall until the b.p. is reached. With amorphous sulphur the conductivity falls as far as 140°–150°, then increases up to 160°–170°, after which temp. it falls continuously to the b.p. B. Kurrelmeyer found that the optical absorption by sulphur crystals is complete in the violet, but relatively low from 500 to $600m\mu$. The photoelectric conductivity is measurable between 400 and $650m\mu$; its maximum, referred to unit incident energy, lies at $470m\mu$. There is strict proportionality between photo-current and light intensity and between photo-current and electric intensity throughout the ranges used. If there is a saturation value of the electric intensity it probably lies above 30,000 volts per cm., and is therefore very much higher than the saturation electric intensity in the diamond and in zincblende. C. Roos found that the conductivity of rhombic sulphur is increased by exposure to X-rays. According to A. Wigand, R. Threlfall and co-workers, the electrical resistance of sulphur is decreased in the presence of moist air. E. Duter, G. E. M. Foussereau, and J. Monckman made observations on the conductivity of molten sulphur; G. Quincke, on the electrical properties of colloidal soln. of sulphur; and C. Roos, on the increase in the conductivity imparted by X-rays. J. J. Thomson observed that the vapour of sulphur has a very small electrical conductivity. R. S. Bartlett studied the resistance of spluttered films of sulphur. According to P. Fischer, mixtures of a large proportion of sulphur with silver and arsenic, sulphides, galena, copper pyrites, and stibnite are non-conducting; but a mixture of sulphur and copper sulphide is a conductor; when this is used as cathode in a soln. of, say, sodium sulphate with cadmium as anode, cadmium sulphide is formed.

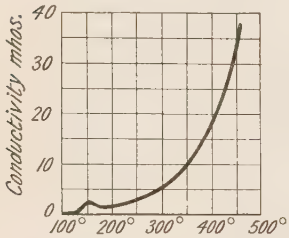


Fig. 30.—Electrical Conductivity of Sulphur

R. Threlfall and co-workers said that the contact **electromotive force** between soluble and insoluble sulphur is between 1–2 volts, and the insoluble form acquires a positive charge. The electric strength of crystallized sulphur exceeds 33,000 volts. per c.c. S. Bidwell made solid cells of sulphur mixed with sulphides of silver or copper compressed between plates of silver and copper—each 3 cms. square—and obtained a current of several micro-amperes. He called them *sulphur cells*. F. W. Küster and W. Hommel found that during the electrolysis of a soln. of a polysulphide both the current and voltage undergo periodic variations due to the deposition of sulphur on the anode. Such electrodes may be regarded as *sulphur electrodes*, just as a platinum plate sat. with oxygen is regarded as an oxygen electrode. According to M. le Blanc, when a thin film of sulphur on a platinum wire is used as cathode in a soln. of potassium hydroxide, it goes into soln. as a polysulphide, S''_n, where the largest observed value of n was 5. When used as anode, no action was observed at all. E. Müller and R. Nowakowsky found that sulphur dissolves at the cathode in 0·1*N*-KOH with a valency of 0·67–0·68. The potential at which the dissolution begins is 0·53 volt measured against a 0·1*N*-calomel electrode. M. G. Levi and E. Migliorini discussed the formation of thiosulphates, and sulphoarsenates by the action of sulphur ions on sulphites, etc. Negative results were obtained with sulphoantimonates, and sulphomolybdates. I. Klemencic studied the reflection of tubes of electric force from sulphur plates. R. Lucas gave −0·59 volt for the **electrode potential** of sulphur against the hydrogen electrode; L. Bruner and J. Zawadsky, −0·545 volt; and L. Rolla, 0·575 volt. D. F. Smith and J. E. Mayer gave for the **reduction potential** and the decrease of free energy at 25°, for $SO_2+4H^{\cdot}=S+2H_2O$, respectively −0·470 volt and −43,350 cals.; and for $SO_4''+8H^{\cdot}=S+4H_2O$, respectively −0·359 volt and –49,700 cals. F. W. Bergstrom gave for the electronegative series in liquid ammonia, Pb, Bi, Sn, Sb, As, P, Te, Se, S, I. F. Hund discussed the potential of S''-ions.

According to L. Boltzmann,[29] the **dielectric constants** of sulphur crystals in the direction of the three axes are respectively 4·773 : 3·970 : 3·811. F. Rosetti, and M. Faraday gave 2·24 for the dielectric constant of sulphur; F. Rosetti, 1·81 (air unity); A. Wüllner, 2·88–3·21; J. E. H. Gordon, 2·5793; J. J. Thomson, 2·4; C. B. Thwing, 2·69; M. Lefebore, 2·7; W. Schmidt, 3·95 for $\lambda=75$ with freshly cast sulphur, and after ageing, 3·90; while R. Fellinger gave respectively 4·05 and 3·60 for $\lambda=\infty$. R. Threlfall and co-workers found for aged monoclinic sulphur 3·162 at 14°; when 1·43 per cent. of insoluble sulphur was present, 3·510; and with 3·75 per cent. of insoluble sulphur, 3·75. For liquid sulphur near its b.p., M. von Pirani gave 3·42 for $\lambda=\infty$. P. Cardani found that for not very intense electric fields, the dielectric constant is between 3·5 and 3·6, but it increases with increasing intensity of the electric field; and R. Threlfall and co-workers found that the constant increases with temp.—the temp. coeff. is 2×10^{-6} per degree. S. Rosental found that there is an abrupt increase in the dielectric constant of sulphur at the moment of solidification. Comparisons of the observed dielectric constant with that calculated from the electromagnetic theory of light, were made by L. Boltzmann, N. N. Schiller, etc. H. Neumann studied the relation between the conductivity and the dielectric hysteresis; by exposure to X-rays or γ-rays, the electrical conductivity is raised but the hysteresis is scarcely affected. J. Dewar and J. A. Fleming found that the dielectric constant of water at —185° is very little affected by the presence of finely divided sulphur. G. L. Addenbrooke studied the relation between the dielectric constant and other physical properties. A. M. Taylor and E. K. Rideal gave $7{\cdot}5\times10^{-18}$ E.S.U. for the **electrical moment** of the S_2-molecule.

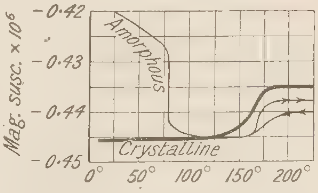


FIG. 31.—Magnetic Susceptibilities of Crystalline and Amorphous Sulphur.

M. Faraday,[30] and T. Carnelley showed that sulphur is diamagnetic. A. P. Wills gave for the **magnetic susceptibility,** $-0{\cdot}77\times10^{-6}$ vol. units; J. Königsberger, $-0{\cdot}9\times10^{-6}$ vol. units; and L. Lombardi, $-0{\cdot}85\times10^{-6}$ vol. units. S. Meyer gave $-0{\cdot}34\times10^{-6}$ mass units at 18°; P. Curie, $-0{\cdot}51\times10^{-6}$ between 15° and 225°; K. Honda, $-0{\cdot}48\times10^{-6}$ mass units between 18° and 300°; and P. Pascal, $-0{\cdot}49\times10^{-6}$ mass units at 16°. M. Owen gave for liquid sulphur $-0{\cdot}485\times10^{-6}$ mass units. T. Ishiwara said that the diamagnetic susceptibility of sulphur shows no discontinuity in passing from rhombic to monoclinic crystals; and the curves give no indication of fusion; but the transformation in the liquid phase is accompanied by a decrease of about 2 per cent. in the diamagnetism, Fig. 31, after which the susceptibility is again constant. There are indications of a reversible transformation at about 80°, which may be due to the presence of an amorphous sulphur, Fig. 31. L. A. Welo, and B. H. Wilsdon calculated values for the magnetic constants. A. Dauvillier, and P. Pascal discussed the diamagnetism and the atomic structure of sulphur. P. Pascal gave -150×10^{-7} for the **atomic susceptibility** of sulphur; and S. S. Bhatnagar and C. L. Dhawan, $16 \cdot 0 \times 10^{-6}$.

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§ 7. The Chemical Properties of Sulphur

Sulphur unites directly with almost all the elements excepting the inert gases, gold, and platinum. J. Thomsen[1] said that the affinity of sulphur for the metals is less than it is for oxygen; and O. Schumann concluded, from observations of the action of hydrogen on the sulphates, of superheated steam on the sulphides, and of hydrogen sulphide on the oxides, that in group I*a* of the periodic table, potassium and sodium have a greater affinity for sulphur than for oxygen; while in group I*b* the affinities of copper and silver for oxygen and sulphur are about equal. With the metals of group II arranged in the order of their at. wt. from magnesium to barium, the affinity for sulphur increases in the same order: magnesium exhibits a greater affinity for oxygen; with calcium, the affinities for sulphur and for oxygen are about equal; whilst strontium and barium display a decidedly greater affinity for sulphur. In group II*b*, the affinities of the metals for sulphur and for oxygen are about equal. The action of hydrogen on the sulphates shows that the affinities of the metals for both metalloids decrease in the order of the at. wts., zinc yielding oxysulphide and cadmium yielding sulphide, whilst mercury yields only metal. In group IV, the affinity of the metals is slightly greater for sulphur than for oxygen. In groups VII and VIII, manganese and iron exhibit equal affinities for sulphur and for oxygen. Nickel and cobalt show a somewhat greater affinity for sulphur. The table exhibits a periodic rise and fall in the affinities of the metals for sulphur. In the first group the affinity decreases from potassium to silver. In the second group, it is almost *nil* with magnesium, it increases from thence to barium, and decreases to mercury. In the third group, aluminium again shows a minimum of affinity for sulphur, which increases in the fourth and fifth groups to arsenic, and then decreases to bismuth. The affinity is once more at a minimum with chromium, and from thence increases throughout the seventh group. The general conclusion is that the strength of affinity for sulphur in relation to that for oxygen, is greatest in metals of highest at. vol. E. Schürmann concluded that when arranged in the order of their affinity for sulphur, the metals form the following series: Pd, Hg, Ag, Cu, Bi, Cd, Sb, Sn, Pb, Zn, Ni, Co, Fe, As, Tl, Mn. In each natural family of elements, the affinity for sulphur increases with the at. wt. Family IV is an exception to this law, as the affinity of sulphur for tin is greater than is its affinity for lead. The members of family III have less affinity for sulphur than their neighbours in family IV, and these again than the corresponding elements with a slightly higher at. wt. in family V. A. Orlowsky concluded that sulphur has the greatest affinity for the alkali metals; and of the heavy metals, its affinity for copper is the greatest; these follow in the order of decreasing affinity Hg, Ag, Fe, and Pb, while the affinity for Pt, Cr, Al, and Mg is small. E. F. Anthon arranged the metals in the order: Ag, Cu, Pb, Cd, Fe, Ni, Co, and Mn. E. Schütz attempted to measure the affinity of sulphur for the metals, and arranged them in descending order: manganese, copper, nickel, iron, tin, zinc, and lead. L. Fernandes studied the variations in the co-ordination forces of the sulpho-salts when oxygen is replaced partially or wholly by sulphur. The union of sulphur with metals whilst under compression was discussed **1.** 13, 18; and A. Buffat made observations on the subject.

W. Ramsay and J. N. Collie,[2] and W. T. Cooke observed no sign of chemical combination between sulphur and **helium**; and Lord Rayleigh and W. Ramsay, and W. T. Cooke, none with **argon**. F. H. Newman studied the absorption of hydrogen and nitrogen by sulphur in an electrical discharge tube. The occlusion of gases by sulphur, and its oxidation by exposure to air, led some of the early workers to suppose that **hydrogen** is an essential constituent of sulphur—*vide supra*, the history of sulphur. H. Moissan, and C. Malus, indeed, found that fresh gas was evolved even after 80 successive fusions. This agrees with the observations of A. M. Kellas, J. N. Lockyer, etc. H. Pélabon said that hydrogen is not absorbed by liquid sulphur. F. H. Newman found that hydrogen, activated by α-rays from polonium, is absorbed by sulphur, even at 0°; the absorption may be due in part to chemical action. G. L. Wendt showed that some hydrogen sulphide is formed when sulphur is exposed to activated hydrogen—*vide infra*, hydrogen sulphides. R. Schwarz and P. W. Schenk, and R. Schwarz and W. Kunser, observed that under the influence of the silent discharge, sulphur vapour is more chemically active than ordinary vapour, but there is no evidence of a depolymerization of the molecule.

As shown by H. Moissan, sulphur exposed to **air** at ordinary temp. is slowly oxidized with the formation of traces of sulphur dioxide. N. Leonhard found that sublimed sulphur generally colours blue litmus red; and it contains 0·02–0·25 per cent. of sulphuric acid. Part of this acid is formed by exposure to air and moisture. Moist sublimed sulphur, free from acid, was distinctly acid after being kept for two weeks in a stoppered bottle, and after 4 years contained 0·2 per cent. of sulphuric and no sulphurous acid; a similar specimen, dried at 100°, contained only 0·0025 per cent. of sulphuric acid after being kept for 4 years. A. G. Doroshevsky and G. S. Pavloff observed that when charcoal is soaked in a soln. of sulphur in carbon disulphide and dried, the sulphur suffers oxidization at 100°. The slow oxidation of moist sulphur to sulphuric acid by exposure to air was observed by R. Maly, J. F. John, and L. Wagenmann; though H. W. F. Wackenroder said that dried milk of sulphur which had been kept for 18 years was free from sulphuric acid. W. Zänker and E. Färber found that the presence of cellulose fibre, or of cotton yarn, accelerates the formation of free sulphuric acid from sulphur exposed to air. They also showed that powdered sulphur from different sources cannot be completely freed from acid by repeated washing, and it therefore appears probable that the latter is continuously formed by the action of air and moisture during the process. Flowers of sulphur contain the greatest amount of free sulphuric acid, roll sulphur much less; colloidal sulphur remains almost as strongly acid after washing as washed flowers of sulphur. The formation of free sulphuric acid from flowers of sulphur or powdered sulphur is most readily demonstrated by washing a quantity of the finely divided material with cold and with hot water, treatment with a little ammonia, and subsequent washing until the water has a neutral reaction; the product is covered with water at 60°–80°, and repeatedly dried and remoistened. The formation of acid is facilitated by passing a current of air. The autoxidation of sulphur occurs more readily in an acid than in a neutral or alkaline medium. W. H. MacIntire and co-workers showed that although the transformation of sulphur added to the soil may be partly a function of the biological content of the soil, yet sulphur may be readily and extensively converted into sulphates by independent chemical action under aerobic or anaerobic or non-sterile conditions of moist contact at normal temp. when ferric oxides and alkaline-earth carbonates are present. It was also shown that the treatment of soils with limestone, dolomite, or magnesite favoured the leaching of the sulphur by rain-water. R. H. Simon and C. J. Schollenberger observed that the rate of oxidation of sulphur in soils is dependent on the grain-size of the material. A. Harpf also noticed that finely divided sulphur is oxidized on exposure to air in light or in darkness; and stated that the assumption made by K. Windisch that the disinfecting property of sulphur on the moulds, formed during the growth of grapes, is due to the formation of sulphur dioxide, produced by the action on the sulphur of active oxygen and hydrogen dioxide generated by the living plants, is thus unnecessary. H. Moissan found that the slow combustion of α-sulphur to sulphur dioxide occurs even at 20° in oxygen confined in sealed tubes; and similar results were obtained with β-sulphur and with amorphous sulphur. The action is slower in air, but traces of sulphur dioxide can be detected after keeping the sulphur for 3 months at 16°–26°. E. Pollacci said that the oxidation of finely divided sulphur in air is accelerated by light; that pure **oxygen** does not effect the oxidation; and that the active oxidizing agent in air is ozone. T. Ewan found that the rate of oxidation of sulphur at 159° is proportional to the sq. root of the press. of the oxygen; but M. Bodenstein and W. Karo found that at 252° the rate of the reaction is directly proportional to the press. of the oxygen, and is roughly proportional to the surface of the sulphur. The rate increases in the ratio 1·87 : 1 for a rise of temp. of 10°. It is therefore concluded that the controlling reaction is a chemical one; that it occurs in the adsorption layer on the surface of the sulphur; and that the sulphur dioxide, which accumulates in the adsorption layer, has no influence on the velocity of the reaction. R. G. W. Norrish and E. K. Rideal found that the reaction proceeds normally up to 305° when the temp. coeff. is 1·63, but above that temp. there is a disturbance due to the secondary formation of the trioxide. The reaction is practically limited to the surface of the sulphur and to the walls of the vessel, and proceeds as well in one case as in the other, indicating that a film liquid of sulphur covers the whole inner surface of the reaction vessel. The speed of the reaction is proportional to the press. of the oxygen; but there is a break in the pressure-velocity curves at 0·41 atm. press. This is taken to mean that the surface reaction is made up of two surface reactions: (*a*) one of which is independent of the press. beyond 0·41 atm. press. and has a temp. coeff. of 1·48, and heat of activation, corresponding with the rupture of the sulphur bonds, of 25,750 cals. at 300°; the other reaction (*b*) has a velocity proportional to the oxygen press. at least as high as one atm. and it has a temp. coeff. of 1·77, and heat of activation of 37,450 cals. at 300°. It is assumed that the sulphur surface contains two types of sulphur molecules, which react along two different courses with the oxygen striking the surface, giving rise to the *A* and *B* reactions. The fact that the *A* reaction finally becomes independent of the oxygen press. indicates that the rate of production of the second allotropic form of sulphur now limits the velocity of the reaction. The temp. coeff. of the interconversion of the two allotropic forms is 1·48. The slow combustion of sulphur in air or oxygen, at about 200°, is attended by a phosphorescence. This phenomenon has been previously discussed. J. Dalton said that in open air sulphur ignites at about 260°; J. Thomson, 293°; T. J. Pelouze and E. Frémy, and J. B. A. Dumas, 150°; W. A. Miller, between 235° and 260°; P. Beyersdorfer and L. Braun, 215°—under conditions where the value for cane sugar is about 410°; and C. M. Tidy gave 115° for rhombic sulphur, and 120° for the prismatic variety. By passing a current of air over sulphur, W. R. Hodgkinson said that the **ignition temperature** cannot be below 300° because a piece of sulphur can be placed on fused nitre (m.p. 339°), and sublimed without ignition; and he did not ignite sulphur vapour at the m.p. of zinc (419°). B. Blount showed that sulphur takes fire at about 270°; at the moment of ignition the flame does not start at the surface of the fused sulphur, but proceeds from its vapour, which has flowed out of the capsule on to the hot plate, the temp. of which is considerably higher than that of the sulphur itself. Later, he found that sulphur vapour takes fire in air at 266°, burning with a blue flame; and on allowing the temp. to fall, the sulphur vapour ceased to ignite in air at 261°. J. R. Hill gave 248° for the ignition temp., and this is very near to J. Dalton's value, 250°. R. H. McCrea and A. Wilson obtained 261° in air at atm. press.; and 257°–264° in oxygen. H. Moissan found that by bubbling oxygen through sulphur melted in an atm. of carbon dioxide, below 482°, sulphur dioxide was formed without any incandescence; when this temp. was reached, the reaction became more vigorous, a slight explosion occurred, followed immediately by incandescence. The ignition point of sulphur in air was found to be 363°; this is raised by the presence of 5 per cent. of sulphur dioxide to 445°, and when 10 per cent. is present, ignition does not occur at 465°. The point of ignition of sulphur vapour in air is much lower than that of liquid sulphur, being about 285°. The subject was discussed by A. G. White. P. Beyersdorfer and L. Braun discussed sulphur-dust explosions in sulphur grinding mills. According to N. Semenoff and G. Rjabinin, as in the case of phosphorus vapour, sulphur vapour can burn in oxygen only between definite limits of press. This press. interval increases with rise of temp. which fixes the press. of sulphur vap. The velocity of ignition, which may be very great, is independent of the oxygen press., and probably depends on the velocity of volatilization of sulphur. It is supposed that, outside these limits of press., the number of active centres which, from the conditions of the experiments, may be either ozone mols. or oxygen atoms, does not reach the necessary value for ignition. The values of the limiting partial press. of oxygen are not altered, as in the case of phosphorus vap., by the presence of foreign gases. Even in the region of effective press. spontaneous ignition takes place only when a very small quantity of ozone is introduced by some means.

W. A. Noyes, and R. Lüpke give experiments to demonstrate that sulphur burns in a given volume of oxygen to produce the same volume of sulphur dioxide. A little sulphur trioxide is, however, produced at the same time. Thus, G. Lunge observed that when sulphur is burned in a glass tube in a slow current of dry air, from 2 to 3 per cent. of the sulphur is oxidized to the trioxide, and if the products of combustion are drawn over ferric oxide, the quantity is increased to 14·17 per cent. W. Hempel found that with sulphur and oxygen under atm. press., the product contains 2·0 per cent. of sulphur trioxide, and 98 per cent. of the dioxide. If the oxygen be at a press. of 40–50 atm., about half is oxidized to the trioxide. J. H. Kastle and J. S. McHargue observed that if the sulphur is burnt in air instead of oxygen about 7 per cent. is converted into the trioxide, and the relative proportions of the oxides produced by the combustion of sulphur in air are not appreciably affected by moisture or increased quantities of carbon dioxide. Moisture is also without influence on the combustion of sulphur in oxygen, but the presence of carbon dioxide causes a slightly larger proportion of the trioxide to be produced. The fact that the quantity of the trioxide formed by the combustion of sulphur in air is so much greater than that produced by combustion in oxygen is considered to be due to the presence of nitrogen. When mixtures of oxygen and nitrogen are employed containing smaller quantities of nitrogen than are present in air, the quantity of the trioxide formed is considerably diminished. It is suggested that the nitrogen acts as a carrier of oxygen, small quantities of one of the higher oxides of nitrogen being formed which effects the oxidation of the sulphur dioxide. H. Giran's data on this subject have been indicated in connection with the heat of combustion of sulphur. The proportion of the total sulphur converted into the trioxide, at different press., is illustrated by Fig. 32. The subject was studied by M. Berthelot, R. J. Nestell and E. Anderson, and J. B. Ferguson. J. Cornog and co-workers found that when sulphur vapour, in the absence of liquid sulphur, is burnt at 460°, about 3·6 per cent. of the gaseous product of combustion is sulphur trioxide. W. C. Young found that sulphuric

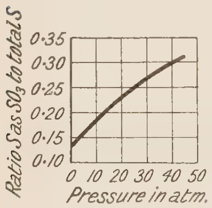

Fig. 32.—Proportion of Sulphur burnt to Trioxide at Different Pressures.

acid is practically the sole product of the oxidation of the sulphur during the combustion of coal-gas; and observations on this subject were made by C. Heisch, M. Dennstedt and C. Ahrens, and G. W. Wigner. When the silent electric discharge is passed through a mixture of the vapour of sulphur and oxygen, much sulphur trioxide is produced; without the discharge, only a little trioxide is formed. J. S. Doting calculated the temp. of the flame of sulphur burning to sulphur dioxide, to be 1025°. According to S. Pagliani, the calculated temp. of combustion of sulphur in the theoretical proportion of air is 1616° at constant press., and 2000° at constant vol. When, however, the combustion takes place in the normal proportion of air used in sulphuric acid works, the theoretical temp. is 900°, whilst the maximum temp., encountered in practice in furnaces working normally, is 550°. In combustion furnaces for the extraction of sulphur from its minerals, the temp. should not be below 250°, which is the minimum temp. at which sulphur burns in a large excess of air. The incomplete utilization of the sulphur in these furnaces is due partly to the large vol. of air required to prevent the temp. rising beyond 300°–340°, above which temp. the sulphur becomes mobile again. The catalytic action of platinum in the combustion of sulphur in organic compounds was studied by F. Pregl, and L. Bermejo and A. Rancano.

C. F. Schönbein was wrong in stating that sulphur is not attacked by **ozone.** A. and P. Thénard said that ozone oxidizes sulphur to the dioxide; and A. Mailfert observed that in the dry state only the dioxide, no trioxide, is formed, and in the moist state only sulphuric acid is produced. Observations were also made by E. Pollacci, T. Weyl, and H. B. Baker and R. J. Strutt. A. Stock and K. Friederici observed that sulphur dissolved in carbon tetrachloride is oxidized to sulphur dioxide, and trioxide. C. Moureu and C. Dufraisse[3] found that in the oxidation of sulphur compounds, etc., by free oxygen, the catalysts can be divided into two classes: (i) anti-oxygenic catalysts which retard the oxidation, and (ii) pro-oxygenic catalysts which accelerate the reaction. In the former case the production of the intermediate compound $A(O_2)$ is prevented. P. W. Edwards discussed explosions in works through the dust of sulphur or of sulphur-lime.

Sulphur is not soluble in **water.** According to W. Spring, the allotropic or colloidal sulphur obtained by H. Debus is really *hydrated sulphur*, $S_8.H_2O$, of sp. gr. 1·9385 at 19°/4°, it loses its water at 80°, and has a slight vap. press. at ordinary temp. He considered that the hydrate is derived not from octahedral sulphur, but from an amorphous, unstable variety which is transformed slowly under ordinary conditions, and more rapidly under press., into soluble sulphur. The oxidation of moist sulphur in air has been already discussed. F. Jones, and J. B. Senderens said that water has no action on sulphur, and that observations to the contrary are due to disturbing effects produced by the action of the alkalies dissolved from the glass containing vessel. E. Pollacci stated that the active agent is not oxygen, but ozone. The best conditions for the action of sulphur on water are a temp. of 35°–40°, and exposure to sunlight. T. Brugnatello and P. Pelloggio said that barium, strontium, and magnesium carbonates favour the action, and that sulphates and thiosulphates are produced, while, in the absence of carbonates, pentathionic acid may be formed. N. R. Dhar observed that when a mixture of powdered sulphur and yellow phosphorus under water at room temp. is treated with air, sulphuric acid is formed. According to J. Böhm, when flowers of sulphur are kneaded in ordinary water, the floating portions removed, and the immersed portions left in an open vessel covered with only a small quantity of water, sulphuric acid is produced, whereas if the flowers of sulphur are kept in spring-water, and the air is excluded, hydrogen sulphide is formed after a short time. Flowers of sulphur which have been kept for a month or longer in well-water, daily changed, immediately produce hydrogen sulphide, and, after a few days, the water, if its volume does not greatly exceed that of the flowers of sulphur, gives with a soln. of a lead salt, a black precipitate, and with barium chloride, a moderate turbidity. In sealed tubes, with flowers of sulphur not very well adapted for the production of hydrogen sulphide, the formation of the gas is permanently hindered by the presence of air, even in small quantity. The same effect is produced by any acid or by phenol; carbon disulphide prevents the action only when the flowers of sulphur have been well mixed with a few drops of it. Flowers of sulphur thus treated, and then freed from the admixed substance, also those which have been boiled or frozen for some days, do not recover the power of immediately producing hydrogen sulphide till they have been digested for some time in spring-water, daily renewed. In distilled water, no hydrogen sulphide is evolved, and even flowers of sulphur highly capable of generating this gas, lose the power of immediately producing it, even in spring-water, if they have been washed with pure water and kept for some time. In distilled water mixed with a little chalk, much less hydrogen sulphide is formed than under similar conditions in spring-water, and a large quantity of chalk prevents the formation of the gas, even under circumstances otherwise favourable. The same is true in a still higher degree for gypsum, and for a considerable quantity of charcoal-powder freed from air by boiling. In the latter case the liquid, which in most cases is faintly alkaline, is strongly clouded by barium chloride. Hydrogen sulphide is also formed on boiling sulphur in water. Well-water thus treated becomes bluish green, and this colour is produced in like manner by distilled water after the addition of chalk. After the gradual decomposition of the carbonate, whereby thiosulphate is formed, the liquid, on cooling, becomes yellowish or colourless. When sulphur is boiled with water in a flask fitted with an upright tube, the sides of the flask become coated with crystalline sulphur, and hydrogen sulphide is given off. The decomposition of this compound, with separation of crystalline sulphur, is effected, as is well known, only by sulphurous acid, according to the equation $2H_2S+SO_2=2H_2O+3S$, which, on the other hand, doubtless represents the formation of the hydrogen sulphide. In acidulated water, no hydrogen sulphide is formed. In sealed tubes containing air, also, no hydrogen sulphide is produced from non-floating flowers of sulphur, even after prolonged boiling; but if they also contain chalk, the gas appears after the oxygen of the air has been consumed in the formation of sulphate. Phenol does not prevent the formation of hydrogen sulphide in boiling water, which takes place, although in comparatively small quantity, at 150° or upwards, even in tubes containing air, and in acid liquids. A. Gutbier noted that traces of polythionic acids and hydrogen sulphide are formed when air-free sulphur vapour is passed into air-free water.

According to E. Mulder, steam, and sulphur at a high temp. react to form pentathionic acid; while V. Meyer stated that thiosulphuric acid is formed. J. Priestley obtained an inflammable air by passing steam over boiling sulphur. According to A. Girard, and C. Geitner, boiling water is decomposed by sulphur, and water is decomposed when heated with sulphur in a sealed tube at 200°; but A. Gélis observed that the little hydrogen sulphide which is produced is due to the presence of impurities in the sulphur, and said that water is not decomposed by sulphur when pure materials are used. Iodine or potassium permanganate favours the reaction. C. F. Cross and A. F. Higgin found that sulphur begins to decompose water at about 95°, producing a trace of hydrogen sulphide: $2H_2O+3S\rightleftharpoons 2H_2S+SO_2$, and the sulphur dioxide may afterwards be oxidized by atm. oxygen; or the reaction may be reversed because when water is distilled from sulphur, sulphur forms in the condensing tubes. O. Ruff and H. Graf believe that C. F. Cross and A. F. Higgin's test for the formation of hydrogen sulphide by treating the distillate with lead acetate gave fallacious results because the formation of lead sulphide may have been produced by the volatilized sulphur. They found that the partial press. of sulphur in an indifferent gas like carbon dioxide, and in steam were almost identical, and this is taken to preclude the occurrence of any measurable reaction. E. Heinze, and E. Noack agree that hydrogen sulphide and polythionic acids can be produced by the action of sulphur on water. According to F. Jones, when sulphur is boiled with water in vessels of platinum or fused silica, hydrogen sulphide and thiosulphuric acid are formed, whilst, in the presence of oxygen, hydrogen sulphide and sulphuric acid are obtained. H. Bassett and R. G. Durrant suggested that hydrogen sulphide and sulphurous acid are not the first products of the hydrolysis of sulphur, but that the reaction is analogous to the hydrolysis of chlorine: $Cl_2+H_2O \rightleftharpoons HCl+HOCl$, so that $2S+2H_2O \rightleftharpoons H_2S+(HO)_2S$. The sulphoxylic acid, H_2SO_2, is very unstable, decomposing into hydrogen sulphide and sulphurous acid in acidic soln., and in alkaline soln. into sulphide and sulphite: $3S(OH)_2 \rightleftharpoons H_2S+2H_2SO_3$—*vide infra.* The thiosulphuric and other sulphur acids are formed by the reaction of the products of the decomposition of sulphoxylic acid with hydrogen sulphide, etc. As indicated in connection with the sulphides of the alkalies and alkaline earths, the alkali hydrolysis of sulphur furnishes polysulphides and thiosulphate, both of which could result from the action of sulphur on previously formed sulphide and sulphite. Attempts to establish the reaction $2S+2H_2O \rightleftharpoons H_2S+(HO)_2S$ have not been successful. The action of moist sulphur on silver and other metals, even at the ordinary temp., is undoubtedly due to slow hydrolysis of the sulphur, which is accelerated by removal of the hydrogen sulphide as insoluble sulphide of the metal. Similarly, soln. of silver salts, or salts of other metals which form very sparingly soluble sulphides, are readily acted upon by sulphur on boiling. A quantitative experiment in which sulphur was digested with metallic silver in presence of chromic acid was in better agreement with reaction $2S+2H_2O \rightleftharpoons H_2S+(HO)_2S$ than with a reaction $3S+3H_2O \rightleftharpoons 2H_2S+H_2SO_3$, since approximately one mol. each of silver sulphide and sulphuric acid were formed. When finely-ground rhombic sulphur is boiled with silver acetate soln., the alteration of the sulphur is very superficial owing to the protective action of the dense, coherent film with which it becomes covered. D. Talmud discussed the effect of acidity on the flotation of sulphur in water.

B. Corenwinder obtained hydrogen sulphide by passing a mixture of steam and sulphur vapour over red-hot pumice-stone, or silica; while E. Gripon obtained a little hydrogen sulphide and a little pentathionic acid by passing steam and sulphur vapour through a red-hot porcelain tube, and J. Meyer, by the action of steam on molten sulphur. G. N. Lewis and M. Randall examined the equilibrium conditions in the system: $2H_2O+3S=2H_2S+SO_2$, and found for the equilibrium constant, $[H_2S]^2[SO_2]=K[H_2O]^2$, $K=0{\cdot}00088$ to $0{\cdot}00232$ at the b.p. of sulphur. M. Randall and F. R. von Bichowsky worked at higher temp., 887° to 137·2°, where free hydrogen is formed by the decomposition of the hydrogen sulphide in $H_2S=H_2+\frac{1}{2}S_2$. According to A. Colson, sulphur deposited on the walls of the flask when conc. soln. of sodium thiosulphate is treated with dil. hydrochloric acid (1 : 10), decomposes water energetically at ordinary temp., while flowers of sulphur decompose boiling water slowly. E. Pollacci said that **hydrogen dioxide** does not oxidize finely divided sulphur.

The action of the **halogens** on sulphur is discussed in connection with the sulphur halides—*vide infra.* K. H. Butler, and M. A. and D. McIntosh observed that sulphur does not react with liquid chlorine. W. Engelhardt[4] observed that colloidal sulphur does not react with iodine. J. B. A. Dumas said that sulphur is soluble in warm **bromine.** E. Beckmann and R. Hanslian, and M. Amadari used **iodine** as a cryoscopic solvent and obtained a mol. wt. S_8. The action was also studied by R. Wright. J. Mori studied the equilibrium of iodine and sulphur in carbon disulphide soln. at 10° and 18°, but obtained solid soln.; no compound was formed. S. Kitashima said that free sulphur is not attacked by **hydrochloric acid** unless in the presence of a large quantity of iron when hydrogen sulphide is formed. G. N. Lewis and co-workers found that aq. soln. of **chlorates** are heated with sulphur to 150°–180°, are slowly reduced owing to the reversible change $2H_2O+3S \rightleftharpoons 2H_2S+SO_2$, where the sulphur dioxide is the active agent; **bromates** are reduced to bromine, and **iodates** to iodine; **perchlorates**, and **periodates** are not acted on at 180°. M. Raffo and co-workers found that when **iodic acid** is mixed with colloidal sulphur, a deep red colour due to free iodine is immediately developed, and subsequently a voluminous, dark red precipitate composed of a mixture of iodine and sulphur separates. There is evidence that the sulphur is oxidized to sulphur dioxide by the iodic acid, the resulting hydriodic acid is oxidized to free iodine by part of the iodic acid, and the latter also oxidizes the sulphur dioxide to sulphuric acid. Under certain conditions, the reaction increases at first with the iodic acid concentration, attains a maximum, and beyond that point diminishes with further increase in conc. According to the conditions, the reaction proceeds until the iodic acid or the sulphur is used up, or until the sulphur separates in gelatinous form.

J. H. Niemann found that sulphur is soluble in warm liquid **hydrogen sulphide ;** and H. Pélabon, that liquid sulphur at 440° freely dissolves hydrogen sulphide, which is liberated with "spitting" as the sulphur solidifies; hydrogen is absorbed at 170°, and more and more is dissolved as the temp. rises to 440°. Even boiling sulphur absorbs hydrogen sulphide at ordinary press. ; and in vacuo, at 440°, the sulphur retains the whole of the absorbed gas. H. Mills and P. L. Robinson found that a suspension of sulphur in aq. ammonia, when saturated with hydrogen sulphide furnishes ammonium pentasulphide. J. B. A. Dumas found that sulphur is soluble in a warm soln. of **barium sulphide,** and J. J. Berzelius, and H. E. Schöne, that an alcoholic soln. of **potassium pentasulphide** dissolves sulphur, which is precipitated by adding water to the sat. soln. F. W. Küster measured the solubility of sulphur in a soln. of **sodium sulphide** between 0° and 50°, and found it to decrease slightly with a rise of temp. The normality, N, of the aq. soln. of Na_2S, and the value of n in the resulting Na_2S_n, were found, at 25°, to be :

N .	4·0	2·0	1·0	0·125	0·0625	0·03125	0·007812
n .	4·475	4·666	4·845	5·225	5·239	5·198	4·456

The solubility thus increases with dilution, having a maximum value with $\frac{1}{16}N$-Na_2S when the ratio $Na_2S : S = 1 : 4$—*vide* alkali sulphides, **2.** 20, 23. J. B. A. Dumas found that sulphur is soluble in **sulphur chloride ;** and H. Rose, that sulphur monochloride dissolves 66·74 per cent. of sulphur at ordinary temp., forming a liquid of sp. gr. 1·7. The solubility was discussed by W. R. Orndorff and G. L. Terrasse, and by L. Aronstein and S. H. Meihuizen. A soln. of sulphur in the monochloride sat. at 20°, does not deposit sulphur when heated to 170° ; and A. H. W. Aten showed that the soln. can then dissolve as much more sulphur as it dissolved at 20°, and that the sulphur is probably present in a special allotropic form—*vide supra,* π-sulphur. A. H. W. Aten found that the fusion temp. of λ-sulphur in sulphur monochloride, representing the solubility, S, of λ-sulphur—in molar percentages—in that menstruum, are :

	−16°	0°	17·9°	55·2°	17·7°	95·6°	86°	103·2°	110·4°	118·8°
S .	4·3	6·0	9·9	28·5	55·4	81·8	81·8	88·4	95	100
Solid phase	α-sulphur						β-sulphur			

F. Sestini, and F. Friedrichs observed that liquid **sulphur dioxide** dissolves a little sulphur. According to R. H. Adie, **sulphuric acid** acts on sulphur, giving off sulphur dioxide at 200° but no hydrogen sulphide. Sulphur reduces sulphuric acid at a high temp. $S+2H_2SO_4=2H_2O+3SO_2$; and as G. N. Lewis and co-workers showed, the reverse reaction is obtained by heating sulphur dioxide and water in a sealed tube at 150°, when sulphur is deposited. This reaction was mentioned by J. Priestley, in a chapter : *On the convertibility of vitriolic acid air into nitriolic acid ;* and it was investigated by M. Berthelot, A. F. de Fourcroy and L. N. Vauquelin, C. Geitner, P. Hautefeuille, J. Tyndall, A. Morren, P. Walden and M. Centnerszwer, C. St. Pierre, and E. Jungfleisch and L. Brunel. H. B. North and J. C. Thomson found that when sulphur and **thionyl chloride** or **sulphuryl chloride** are heated in a sealed tube at from 70° to 180°, the formation of sulphur dioxide and sulphur monochloride begins at 150°. W. Prandtl and P. Borinsky found that **pyrosulphuryl chloride** is without action on sulphur in the cold, but when heated, sulphur monochloride distils over.

The chemical action of activated **nitrogen** on sulphur has been previously discussed, and it follows on the lines indicated in connection with activated hydrogen by F. H. Newman, and G. L. Wendt. A. A. Zimmermann discussed the union of sulphur and nitrogen in the electric discharge. E. C. Franklin and C. A. Kraus found sulphur to be soluble in liquid **ammonia ;** C. Hugot said that 3 to 4 c.c. of the liquid dissolves a gram of sulphur ; O. Ruff, that, between —34° and —84°, liquid ammonia dissolves 39 per cent. of sulphur ; and O. Ruff and L. Hecht gave for the solubility, *S*, in grams of sulphur per 100 grms. of soln. :

	−78°	−20·5°	0°	16·4°	30°	40°
S . .	38·6	38·1	32·34	25·65	21·0	18·5

H. Boerhaave noted the solvent action of aqua ammonia on sulphur, and G. Calcagni found that 100 c.c. dissolves 1·367 grms. of sulphur—*vide* ammonium sulphides, **2**. 20, 24 ; and **8**. 49, 20. W. P. Bloxam observed no reaction between sulphur and a boiling soln. of ammonia ; when the mixture is heated in a sealed tube, polysulphide, thiosulphate, and traces of sulphite, but no sulphate, were formed. F. W. Bergstrom found that sulphur reacts readily with an ammoniacal soln. of the **amides** of lithium, potassium, calcium, barium, and magnesium. T. Curtius, and C. A. L. de Bruyn noted the solvent action of **hydrazine** and its hydrate on sulphur. T. W. B. Welsh and H. J. Broderson found that at room temp. 100 grms. of anhydrous hydrazine dissolve 54 grms. of sulphur with decomposition. According to F. Ephraim and H. Piotrowsky, sulphur readily dissolves both in hydrazine and its hydrate, giving a dark brown soln., which on pouring into water deposits sulphur. At the ordinary temp., anhydrous hydrazine dissolves about 60 per cent. of its weight of sulphur. After a short time a reaction occurs according to the equation : $N_2H_4+2S=N_2+2H_2S$, nitrogen being evolved and an unstable hydrazine hydrosulphide remaining in soln. Observations were also made by J. Meyer and J. Jannek, A. Gutbier and R. Emslander, and Wo. Ostwald and I. Egger. According to C. C. Palit and N. R. Dhar, 13 and 26 per cent. **nitric acid** have no action on sulphur at ordinary temp. H. Zieler observed no reaction with nitric acid up to 40 per cent. HNO_3, and with boiling 50 per cent. acid, a feeble reaction occurred. P. F. Frankland and R. C. Farmer found that sulphur is slightly soluble in liquid **nitrogen peroxide;** and J. B. A. Dumas found that warm **nitrogen trichloride,** and **phosphorus trisulphide** dissolve some sulphur. L. Delachaux represented the reaction with phosphine by $2PH_3+nS=3H_2S+P_2S_{n-3}$, which occurs above 320°. T. Karantassis observed that with a soln. of sulphur in carbon disulphide, **phosphorus triiodide** forms *phosphorus tetracosisulphotriiodide*, $PI_3.3S_8$. F. Jones found that **phosphine** acts on sulphur in diffused daylight or better in sunlight ; the action is slower than with **arsine.** The metalloid sulphide and hydrogen sulphide are formed ; with **stibine,** some hydrogen is produced by a secondary reaction. G. Vortmann and C. Padberg found that **antimony trichloride** is not altered when boiled with water and sulphur. G. Vortmann and C. Padberg found that **arsenic trioxide or pentoxide** is not altered when boiled with water and sulphur. V. Auger observed that sulphur forms compounds with **arsenic triiodide,** and **antimony triiodide** (*q.v.*). The reactions were studied by K. Schneider. F. E. Brown and J. E. Synder found that at 0°, 20°, 45°, and 65°, 100 grms. of **vanadium oxytrichloride** dissolve respectively 3·307, 5·995, 13·103, and 30·73 grms. of sulphur ; above 80°, the soln. becomes viscous, and, after a time, it solidifies, giving off sulphur dioxide. O. Ruff and H. Lickett represented the reaction $2VOCl_3+S=2VCl_3+SO_2$.

The reaction between sulphur and **carbon** was discussed **6**. 39, 40. The subject was studied by A. B. Berthollet, C. A. Berthollet, L. N. Vauquelin, etc. J. P. Wibaut found that after heating a mixture of sugar charcoal and sulphur to bright redness, the 3 to 6 per cent. of sulphur which remains cannot be extracted with solvents, and may be chemically combined, or only adsorbed. J. P. Wibaut and E. J. van der Kam found that only the amorphous forms of carbon are able to fix sulphur when the two elements are heated in a closed tube at 500° to 600°. E. H. Büchner showed that sulphur is insoluble in liquid **carbon dioxide.** P. Winternitz, and J. B. Ferguson studied the equilibrium conditions in the reaction: $CO_2+\frac{1}{4}S_2 \rightleftharpoons CO+\frac{1}{2}SO_2$. The latter found that at 1000° and 1200°, using broken porcelain, or platinized porcelain as contact agents, $[CO_2][S_2]^{\frac{1}{4}}=K[CO][SO_2]^{\frac{1}{2}}$; and $\log K=5659T^{-1}-0{\cdot}6915\log T+0{\cdot}00030T-0{\cdot}000000034T^2-0{\cdot}872$; and for the change in the free energy, $\delta F=-25915+1{\cdot}375T\log T-0{\cdot}0014T^2+0{\cdot}000000155T^3+3{\cdot}99T$; and at 25°, $F=-69761$ cals. At 1000°, $\log K=1{\cdot}75$; at 1200°, 1·15; at 1400°, 0·69; and at 1500°, 0·50. Probably small quantities of carbonyl sulphide are formed; and G. N. Lewis and W. N. Lacey studied the equilibrium conditions in the reaction between **carbon monoxide** and liquid sulphur—**5.** 39, 29—$CO+S=COS$, in which are also involved: $CS_2=CS+S$, and $2COS=CO_2+CS_2$. The equilibrium constant for $[COS]=K[CO]$ is $K=435$ at 260°, and 201 at 302°. R. Schwarz and P. W. Schenk observed that sulphur vapour is more chemically active towards carbon monoxide when the vapour is exposed to the silent electric discharge. There is no evidence of a depolymerization of the molecule.

The most commonly used solvent for sulphur is **carbon disulphide.** Observations were made by A. Payen, C. J. St. C. Deville, A. Cossa, J. W. Retgers, G. Gore, etc. In the following, the solubility S represents the number of grams of α-sulphur dissolved by 100 grms. of soln.; the results below −60° are by H. Arctowsky, the others are by A. Étard.

	−110°	−100°	−80°	−60°	−40°	−20°	−10°	0°
S . .	3·0	3·5	4·0	5·5	6·0	10·5	13·5	18·0
	10°	20°	25°	30°	40°	60°	80°	100°
S . .	23·0	29·5	33·5	38·0	50·0	66·0	79·0	92·0

J. W. Retgers gave 26·4 at 10°. By definition, μ-sulphur is insoluble in carbon disulphide. Some varieties of α-sulphur are not entirely soluble in that menstruum, presumably owing to the presence of μ-sulphur. For instance, E. Tittinger reported neither ordinary roll sulphur, nor flowers of sulphur to be completely soluble in carbon disulphide; while precipitated sulphur is completely soluble in five times its weight of that solvent. According to C. J. St. C. Deville, the first of the following data refers respectively to the solubility of sulphur, in grams, per 100 grms. of carbon disulphide, and the second represents the fraction of the original weight which is insoluble in that menstruum: Sicilian α-sulphur, 33·5, 0·000; recently prepared rhombic sulphur crystallized in a dry way, 41·5, 0·029; the same after 8 years, 33·0, 0·004; the same after 9 years, —, 0·020; and the same after 15 years, —, 0·051; recently prepared red needles, 38·2, 0·023; recently prepared soft yellow sulphur, —, 0·353; the same after 2 years, 31·6, 0·157; recently prepared soft red sulphur, 37·4, 0·157; the same after 5 years, —, 0·181; flowers of sulphur, 35·1, 0·113 to 0·234; and roll-sulphur (outside), —, 0·029 to 0·073. M. Amadori said that 100 grms. of carbon disulphide dissolve 53·2 grms. of sulphur at 25°—*i.e.* 34·76 grms. per 100 grms. of soln. According to C. E. Guignet, if a layer of carbon disulphide be poured over soln. of sulphur in that solvent, and thereon a layer of oil, absolute alcohol, ether, benzene, or petroleum, the solvents diffuse into one another and sulphur crystallizes out of the soln.

C. A. L. de Bruyn found the solubility of α-sulphur in absolute **methyl alcohol** to be 0·028 grm. per 100 grms. of solvent at 18·5°; and with absolute **ethyl alcohol,** 0·053 grm. at 18·5°; J. J. Pohl gave 0·051 grm. at 15°; and A. Payen, 0·42 at the b.p. Other observations were reported by L. L. F. Lauraguais, A. Payen and J. B. A. Chevallier, P. T. Meissner, and T. J. Pelouze and E. Frémy. J. N. Brönsted found for β-sulphur, 0·066 per cent. solubility in ethyl alcohol, and α-sulphur, 0·052 per cent. at 25·3°. H. Prinz said that no chemical action occurs at 200°; and A. G. Bloxam that the soln. in hot alcohol first deposits β-sulphur on cooling. A. Gerardin found the solubility of α-sulphur in 100 grms. of **amyl alcohol** to be

1·5, 2·15, and 2·65 grms. respectively at 95°, 110°, and 112°; and for liquid sulphur, 2·65, 3·0, and 5·3 grms. at 112°, 120°, and 131° respectively. Sulphur is soluble in **hexyl alcohol.** J. W. Klever found that **glycerol** dissolves 0·10 per cent. of sulphur; P. A. Cap and M. Garot, that 100 parts of glycerol dissolve 0·05 part of sulphur; and A. M. Ossendowsky, 0·14 grm. at 15·5°. A. Cossa found that 100 grms. of **ethyl ether** at 23·5° dissolve 0·97 grm. of α-sulphur; and J. N. Brönsted, 0·080 grm. at 0°, and 0·200 grm. at 25·3°, while for β-sulphur these numbers are 0·113 grm. at 0°, and 0·253 grm. at 25·3°. J. M. Favre also measured the solubility of sulphur in ether. R. Delaplace found that 0·188 grm. of sulphur is dissolved by 100 grms. of anhydrous ether at 13°. J. Meyer also found that β-sulphur is more soluble than α-sulphur in ether. W. Alexéeff noted the reciprocal solubility of ether in sulphur. W. Eidmann showed that sulphur is soluble in **acetone;** and W. Herz and M. Knoch found that 100 c.c. of acetone dissolve 65 millimols of sulphur at 25°, and 100 grms. of a mixture with water and 95·36, 90·62, and 85·38 grms. of acetone dissolve respectively 45·0, 33·0, and 25·3 millimols of sulphur. Sulphur is also soluble in **aldehyde.** J. W. Retgers found that 100 grms. of **methylene iodide** at 10° dissolve 10 grms. of sulphur; and melted sulphur is miscible with hot methylene iodide. A. Étard showed that 100 grms. of a soln. of **ethylene dibromide** contain, at

	0°	10°	20°	40°	60°	80°	100°
Sulphur .	1·2	1·7	2·3	4·4	8·4	16·5	36·5 grms.

J. N. Brönsted observed that 100 c.c. of a sat. soln. in **ethyl bromide** contain 0·852 grm. of β-sulphur at 0°, and 1·676 grms. at 25·3°; or 0·611 grm. of α-sulphur at 0°, and 1·307 grms. at 25·3°. Sulphur is also soluble in **ethyl chloride.** K. A. Hofmann and co-workers found that, at 25°, 100 grms. of **tetrachloroethane** dissolve 1·23 grms. of α-sulphur and 100 grms. of **ethylene dichloride,** 0·84 grm. J. H. Hildebrand and C. A. Jenks found that 100 grms. of ethylene dichloride dissolve 0·826 grm. α-sulphur at 25°; 1·380 grms. at 40°; 5·43 grms. at 79°; and 99·7 grms. at 97·5°; **dichloroethane,** 1·28 grms.; **pentachloroethane,** 1·2 grms.; **tetrachloroethylene,** 1·53 grms.; and **trichloroethylene,** 1·63 grms., while D. H. Wester and A. Bruins gave 1·19 grms. at 15°. J. J. von Bogusky found that above 134·2°, sulphur is miscible with **benzyl chloride** in all proportions, but below that temp., the mixture separates into two layers—the upper layer has 0·99 grm. of sulphur per 100 grms. of soln. at 0°; 19·89 grms. at 99·1°; 37·29 grms. at 118° and 56·20 grms. at 132·2°; while the lower layer has 90·62 grms. at 109·6° and 72·23 grms. at 134·2°. W. Alexéeff gave 116° for the critical soln. temp. of sulphur and **chlorobenzene.** K. A. Hoffmann found that 100 grms. of **carbon tetrachloride** dissolve 0·86 grm. of sulphur at 25°. J. H. Hildebrand and C. A. Jenks found that 100 grms. of carbon tetrachloride dissolve 0·339 grm. of α-sulphur at 0°; 0·831 grm. at 25°; 1·155 grms. at 35°; 1·564 grms. at 45°; and 2·008 grms. at 54°. R. Delaplace found that 0·645 grm. of sulphur is dissolved by 100 grms. of carbon tetrachloride at 15·5°. A. von Bartal found that sulphur reacts with **carbon tetrabromide** in a sealed tube at 180°–195°, forming carbothiohexabromide, $C_2Br_4S_2$, carbon disulphide, bromine, and sulphur monobromide, but forming, according to G. Gustavson, thiocarbonyl chloride and sulphur monochloride. H. V. A. Briscoe and co-workers obtained only sulphur monobromide, carbon disulphide, bromine, and carbon. J. Meyer noted that β-sulphur is more soluble than α-sulphur in chloroform. B. Rathke also noted the solubility of sulphur in this menstruum. A. Cossa observed that 100 grms. of chloroform at 22° dissolve 1·21 grms. of sulphur. J. N. Brönsted found that at 12·25° and 192·29°, 100 grms. of **chloroform** dissolve respectively 0·744 and 0·918 grm. of sulphur; and at 0°, 15·5°, and 40°, chloroform dissolves respectively 1·101, 1·658, and 2·9 per cent. of β-sulphur, and 0·788, 1·253, and 2·4 per cent. of α-sulphur. R. Delaplace found that 0·874 grm. of sulphur is dissolved by 100 grms. of chloroform at 15°. W. Alexéeff noted the reciprocal solubility of chloroform in sulphur. C. B. Mansfield found sulphur to be soluble in **bromoform,** and M. Amadori said that it dissolves 3·64 per cent. of sulphur at 5·6°. V. Auger observed that sulphur forms addition products with **iodoform, and tetraiodoethylene.** Sulphur is also soluble in warm **chloral,** in **bromal,** and in **iodal.** G. Bruni and C. Pellizzola studied the system sulphur and **p-dichlorobenzene.** Sulphur is soluble in **mercury methide;** and in **ethyl nitrate,** from which soln. it is not precipitated by water. J. A. Wilkinson and co-workers found the solubilities of rhombic and monoclinic sulphur in **$\beta\beta'$-dichlorodiethylsulphide** to be the same over the range 13·82°–128°; and the solubility-f.p. curve is shown in Fig. 33. Below 78°, the solid phase is rhombic sulphur, and above that temp., monoclinic sulphur. The solubility of amorphous sulphur is below 0·14 per cent. at temp. below 120°—at which temp. sulphur melts and passes into soln. Sat. soln. of sulphur in this solvent contain 7·6 per cent. of sulphur at 80°; 11·3 per cent. at 90°; 17·5 per cent. at 100°; and 21·0 per cent. at 104°. B. Rathke found sulphur to be soluble in **ethyl sulphide ;** and it is dissolved by **ethyl and butyl hydrosulphides ;** it is also soluble in **cacodyl oxide** and in warm **allyl thiocyanate** –W. Alexéeff gave 124° for the critical soln. temp. of allyl thiocyanate and sulphur. A. Naumann found sulphur is slightly soluble in **benzonitrile** at ordinary temp., but more soluble at a higher one.

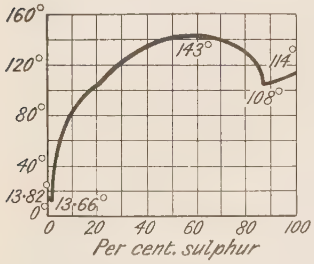

FIG. 33.—Freezing-point Curve of Sulphur and $\beta\beta'$-dichlorodiethylsulphide.

C. T. Liebermann observed that sulphur is dissolved by warm, conc. **acetic acid,** but only a trace is dissolved by the dil. acid. M. Rosenfeld found sulphur to be readily dissolved by boiling **acetic anhydride,** and this, according to H. Prinz, without chemical action. J. N. Brönsted showed that 0°, **ethyl formate** dissolves 0·028 per cent. of β-sulphur, and 0·019 per cent. of α-sulphur. A. Naumann observed that sulphur is sparingly soluble in **methyl acetate,** and soluble in **ethyl acetate,** while J. M. Favre observed that acetic ether dissolves 6 per cent. of sulphur. Sulphur is insoluble in **valeric acid,** and in **amyl valerate.** G. Vulpius found sulphur to be soluble in a soln. of **stearic acid ;** while C. B. Gates noted that 100 c.c. of **oleic acid** dissolve 6·7 grms. of sulphur in six days. A. Michael observed that a cold alcoholic soln. of **sodium ethyl malonate** dissolves sulphur, with a slight chemical action. Sulphur is slightly soluble in a boiling conc. soln. of **thiocyanic acid** from which most separates out on cooling.

G. Capelle, and F. W. O. de Coninck found that when **acetylene** is passed over molten sulphur, in the absence of air, the chief products are hydrogen sulphide, carbon disulphide, and thiophene. H. V. A. Briscoe and J. B. Peel, and J. B. Peel and P. L. Robinson also noted the production of thiophene as well as carbon disulphide between 325° and 650°; V. Meyer and T. Sandmeyer also noted the production of thiophene in the reaction. Sulphur is soluble in **valerylene.** A. Étard found that 100 grms. of a **hexane** soln. of sulphur contain at

	−20°	0°	20°	40°	80°	120°	160°	180°
Sulphur .	0·07	0·16	0·25	0·55	1·7	4·4	7·2	8·2 grms.

J. H. Hildebrand and C. A. Jenks found that 100 grms. of **heptane** dissolve 0·124 grm. of α-sulphur at 0°; 0·362 at 25°; 0·512 grm. at 35°; 0·698 grm. at 45°; and 0·926 grm. at 54°. A. Payen, C. B. Mansfield, A. Cossa, and A. Étard observed that sulphur is soluble in **benzene ;** the last-named gave for 100 grms. of the soln., at

	0°	20°	40°	60°	80°	100°	120°	130°
Sulphur .	1·0	1·7	3·2	6·0	10·5	17·5	29·0	36·0 grms.

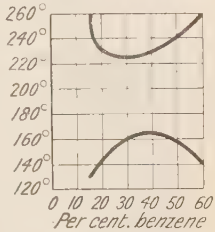

Fig. 34.—Reciprocal Solubility of Sulphur and Benzene.

M. Amadori said that 100 grms. of solvent dissolves 2·15 grms. of sulphur at 25° —*i.e.* 2·9 grms. per 100 grms. of soln.; and R. Delaplace, 1·582 grms. of sulphur per 100 grms. of solvent at 15°. J. Böseken, and C. Friedel and J. M. Crafts observed that boiling benzene in the presence of aluminium chloride reacts with sulphur, forming diphenyl sulphide, thianthrene, etc. D. L. Hammick and W. E. Holt studied the equilibrium conditions in the system: $S—C_2H_6$. W. Alexéeff gave 163° for the critical soln. temp. with benzene and sulphur. J. H. Hildebrand and C. A. Jenks found that 100 grms. of benzene at 25° dissolve 2·074 grms. of α-sulphur; and 5·165 grms. at 54°. H. R. Kruyt observed that benzene and sulphur are completely miscible above 160°, and below 226°. The miscibility curves above and below these temp. are illustrated by Fig. 34. J. Böseken represented the reaction with boiling benzene in the presence of aluminium chloride by: $8S+6C_6H_6+3AlCl_3=4H_2S+2(C_6H_5)_2S(AlCl_3)+(C_6H_4)_2S_2.AlCl_3$. According to J. N. Brönsted, at 18·6° and 25·3°, benzene dissolves respectively 2·064 and 2·335 per cent. of β-sulphur, and 1·512 and 1·835 per cent. of α-sulphur. J. Meyer also noted that β-sulphur is more soluble than α-sulphur in benzene. J. H. Hildebrand and C. A. Jenks found that 100 grms. of **toluene** at 0° dissolve 0·987 grm. of α-sulphur; 2·018 grms. at 25°; 2·722 grms. at 35°; 3·620 grms. at 45°; and 4·85 grms. at 54°. R. Delaplace found 1·857 grms. of sulphur are dissolved by 100 grms. of toluene at 20°. W. Alexéeff gave 180° for the critical soln. temp. with sulphur and toluene. H. R. Kruyt observed that with sulphur and toluene, the limits of complete miscibility lie between 180° and 220°, and the curves are similar in type to those of Fig. 34. J. K. Haywood made observations with mixtures of sulphur and toluene. A. Smith and co-workers, and H. R. Kruyt studied the system sulphur and **triphenylmethane**; the solubility curves are shown in Fig. 7, and the miscibility curves are similar in type to Fig. 34, with the limits of complete miscibility between 145° and 200°. J. K. Haywood made observations with mixtures of sulphur and **xylene.** H. R. Kruyt found that the system sulphur and *m*-xylene gives curves in which the components are not completely miscible within the limits of temp. employed. J. H. Hildebrand and C. A. Jenks found that 100 grms. of *m*-xylene dissolve 1·969 grms. of α-sulphur at 25°; and 3·604 grms. at 45°. With sulphur and **ethylbenzene,** a chemical reaction at about 200° interferes with the results. H. R. Kruyt, and D. L. Hammick and W. E. Holt studied the system sulphur and benzoic acid; and K. Schneider, the action of sulphur on various organic iodides. Sulphur is soluble in **ligroin**, etc. N. T. de Saussure found that 12 parts of hot **petroleum** from Amians dissolved one part of sulphur: C. B. Mansfield found sulphur to be soluble in ligroin. For the solubility of sulphur in grams per 100 parts of **coal-tar oil,** J. Pelouze gave for oils of different sp. gr. and b.p.:

Fraction							
Sp. gr.	B.p.	15°	30°	50°	100°	120°	130°
0·870	80°–100°	2·1	3·0	5·2	15·2	—	—
0·880	85°–120°	2·3	4·0	6·1	18·7	27·0	—
0·882	120°–200°	2·5	5·3	8·3	23·0	32·0	38·7
0·885	150°–200°	2·6	5·8	8·7	26·4	38	43·8
1·010	210°–230°	6·0	8·5	10·0	52·5	∞	∞
1·020	220°–300°	7·0	8·5	12·0	54·0	∞	∞

A. Payen found that 1·35 and 16·2 grms. of sulphur dissolve in 100 grms. of **turpentine** at 16°, and at the b.p. respectively. Sulphur dissolves in hot **styrene**, and separates from the soln. on cooling. A. Cossa found that 100 grms. of **phenol** dissolved 16·4 grms. of sulphur at 164°. A. Smith and co-workers found that mixtures of sulphur and 100 grms. of phenol could be heated until they were homogeneous, and on cooling, a cloudiness appeared at

	89·5°	138°	160·5°	167·5°	175°
Sulphur .	9·1	19·9	28·6	32·4	36·5 grms.

Similarly with 100 grms. of **β-naphthol,** a cloudiness appeared at

	118°	143·5°	157°	164°	163°
Sulphur .	34	59·3	97·4	209·7	300 grms.

Sulphur is slightly soluble in cold **creosote,** but one part of sulphur dissolves in 2·6 parts of boiling creosote. A. Cossa, V. Merz and W. Weith, J. Fritzsche, K. A. Hofmann, O. Hinsberg, and J. A. Barral found that sulphur is very soluble in warm **aniline,** but sparingly soluble in the cold. W. Alexéeff gave 138° for the critical soln. temp. with aniline and sulphur. A. W. Hofmann, I. Cerut, and E. Beckmann and W. Gabel found that **quinoline** dissolves sulphur, but a reaction sets in with the evolution of hydrogen. D. L. Hammick and W. E. Holt studied equilibria in the systems sulphur and quinoline, sulphur and **pyridine,** and sulphur and **p-xylene.** With pyridine as solvent, and a vulcanized rubber membrane, L. Kahlenberg was able to separate, by dialysis, sulphur from cane sugar, silver nitrate, or lithium chloride. J. W. Klever found that 100 grms. of **nicotine** at 100° dissolve 10·6 grms. of sulphur. Sulphur also dissolves in **coniine.** Sulphur is soluble in hot **oil of copaiba,** hot **oil of caraway,** hot **oil of mandarin,** hot **oil of amber,** hot **resin oil,** and **hot caoutchouc.** C. S. Venable and C. D. Greene studied the solubility of sulphur in **rubber.** W. J. Kelly and K. B. Ayers said that the distribution of sulphur between unvulcanized rubber and amyl or *n*-butyl alcohol obeys Henry's law. The sulphur is present in the rubber in a state of soln. and not of adsorption. D. F. Twiss and F. Thomas found μ-sulphur slightly more active than λ- or π-sulphur as a vulcanizing agent for caoutchouc. P. Bary and L. Weydert concluded that ordinary vulcanized caoutchouc is an equilibrium mixture, and that combined sulphur is set free on diminishing the osmotic press. of the free sulphur. The reaction of vulcanization is represented as $C_{10}H_{16}+S_2 \rightleftharpoons C_{10}H_{16}S_2$, but the numerical data obtained are not in agreement with the ordinary law of mass action, whatever hypothesis may be adopted as to the degree of polymerization of the hydrocarbon. The conclusion drawn is that the hydrocarbon molecules having polymerized by union at the double linkings, on vulcanization sulphur first becomes attached only to the terminal double linkings of a chain; further vulcanization, therefore, can only occur after depolymerization. Wo. Ostwald, H. Pohle, and W. E. Glancy and co-workers studied the rate of combination of sulphur with rubber in the formation of vulcanite; A. T. McPherson and co-workers, the density and electrical properties of the system sulphur-rubber. G. S. Whitby and H. D. Chataway studied the action of sulphur when heated with **linseed oil.** J. J. Pohl found that linseed oil dissolves the following percentage amounts of sulphur: 0·630 per cent. at 25°; 1·852 at 60°; 2·587 at 95°; 4·935 at 130°; and 9·129 at 160°; while J. Pelouze observed that 100 parts of **olive oil** of sp. gr. 0·885 dissolved the following parts of sulphur: 2·3 at 15°; 5·6 at 40°; 20·6 at 65°; 25·0 at 100°; 30·3 at 110°; and 43·2 at 130°. D. H. Wester and A. Bruins found that at 45°, 100 grms. of anhydrous **lanoline** dissolve 0·38 grm. of sulphur.

For the action on various hydrocarbons, *vide infra*, hydrogen sulphide. R. F. Marchand studied its action on sugar. The action of sulphur on *n*-octane, octylene, indene, hydrindene, *cyclo*-pentadiene, and α-methylnaphthalene, was investigated by W. Friedmann; on sulphones, by J. Böseken; terpenes, by P. P. Budnikoff and E. A. Schiloff; *cyclo*-hexyl chloride, by A. Mailhe and M. Murat; hydrocarbons—diphenylmethane, and fluorene—by L. Szperl and T. Wierusz-Kowalsky; organo-magnesium compounds, by H. Wuyts and G. Cosyns; amines—toluidine—by H. H. Hodgson, H. H. Hodgson and A. G. Dix, and L. Gattermann; diphenyl, and anthraquinone, by E. Beckmann and

R. Hanslian. The catalytic activity of sulphur compounds in the autoxidation of various organic compounds—benzaldehyde, analdehyde, styrene, turpentine, linseed oil—and sodium sulphite—was studied by G. Moureu and co-workers. H. Freundlich and G. Schikorr found that colloidal sulphur hastens the conversion of maleic acid into fumaric acid.

The action of sulphur on the **metals** and **metalloids** is indicated in connection with the respective sulphides, etc.; similarly also with the metal oxides. According to A. E. Wood and co-workers,[5] the corrosive action on metals of naphtha soln. of sulphur, mercaptans, hydrogen sulphide, alkyl sulphates, sulphonic acids, etc., increases in presence of water. In some cases, this is due to ionization, but in other cases, as with free sulphur, it is due apparently to the formation of anodic and cathodic areas. A mercaptan soln. yields with most metals a mercaptide which is decomposed on heating, yielding sulphide. The affinity of metals for sulphur was discussed by K. Jellinek and J. Zakowsky, C. Frick, and W. Guertler—*vide infra*, hydrogen sulphide. T. W. and W. T. Richards tried to measure gravimetrically the force of chemical affinity at a distance of about 0·001 mm. between the sulphur and the oxides of silver, copper, iron, zinc, and magnesium. In no case did the attractive force amount to 0·1 mgrm.; and it was concluded that the force of chemical affinity must decrease very rapidly as the distance between the attracting atoms increases. W. P. Jorissen and C. Groeneveld studied the reaction between sulphur and iron, and sulphur and aluminium. A. Frumkin observed that when drops of a soln. of sulphur in a light volatile solvent—like ethyl ether, benzene, and light petroleum—are dropped on to a surface of clean mercury, the first drops spread out very rapidly and subsequent drops more slowly until finally a stage is reached where addition of another drop does not cause further spreading. At this stage, the mercury is covered with a unimolecular layer of sulphur, and the area of the surface occupied by each sulphur atom is of the order of magnitude of the cross-section of a mercury atom. The linking between the mercury and sulphur atoms would therefore seem to be of the same type as in a chemical compound of these elements. K. Schneider studied the action of sulphur on germanium and stannic iodides.

The action of **alkali hydroxides** on sulphur has been previously discussed—**2**. 20, 21. C. Fahlberg and M. W. Iles said that when potassium hydroxide is fused with sulphur, sulphide and thiosulphate are formed; with an excess of the alkali, only sulphite and sulphate are formed. M. J. Fordos and A. Gélis said that with boiling alkali-lye and sulphur, more thiosulphate is formed than corresponds with the reaction: $3K_2O+nS+H_2O=2K_2S_{n-2}+K_2S_2O_3+H_2O$; alkaline earth hydroxides give similar results. J. B. Senderens said that the equation represents a limiting case applicable only to conc. soln.; with dil. soln., the polysulphide is decomposed into thiosulphate and hydrogen sulphide. According to H. V. Tartar, the primary reaction of sulphur with potassium hydroxide in hot aq. soln. takes place in accordance with the equation: $6KOH+8S=2K_2S_3+K_2S_2O_3+3H_2O$. When sulphur is used in excess, a secondary reaction occurs, in which it combines with the trisulphide to form the pentasulphide. Potassium tetrasulphide is perhaps formed as an intermediate product. A variation in temp. (below 100°) and conc. does not alter the nature of the reaction. H. Pomeranz supposed that some hydrosulphite is formed. With solid alkali, and sulphur, E. Filhol and J. B. Senderens gave 14·4 Cals. for the heat of the reaction; but in dil. soln., no heat is developed. With solids, the reaction proceeds by simple trituration; but it is slow in soln., and this the more, the less the conc. R. Boyle observed that while neither sulphur nor potassium carbonate is soluble in alcohol, yet the spirit of wine in contact with a mixture of sulphur and potassium carbonate "will in less than an hour, and sometimes in less than a quarter of that time, dissolve enough of this matter to be richly colour'd by it, and this without the help of external heat." T. L. Davis and J. W. Hill obtained a similar result. J. K. Haywood, S. J. M. Auld, and R. W. Thatcher studied the reactions which occur when mixtures of **calcium hydroxide**, water, and sulphur are boiled for different periods of time. The soln. contains chiefly calcium pentasulphide and thiosulphate together with some sulphite and sulphate. L. Guitteau investigated the action of **barium hydroxide,** sulphur, and boiling water. According to J. B. Senderens, the reaction with sulphur when boiled with **cuprous and cupric oxides,** or with **silver oxide,** can be symbolized: $4Ag_2O+4S=3Ag_2S+Ag_2SO_4$; and $3Ag_2SO_4+4S=3Ag_2S+4SO_3$. The sulphate persists even after long boiling when the **oxides of cadmium, mercury, lead, bismuth, or nickel** is similarly treated; **cobalt oxide** is attacked more slowly than **nickel oxide,** and in both cases a thiosulphate is formed which decomposes into the sulphate; **manganese hydroxide,** and **magnesium oxide** form thiosulphates; and when **chromic oxide** or **mercurous oxide** is triturated with sulphur, inflammation may occur with the formation of sulphur dioxide, sulphate, and sulphide. C. Brückner found that when a mixture of chromic oxide and sulphur is heated in air, the oxide is not changed; **chromic anhydride** inflames, and forms chromic oxide together with a little chromium sulphide—*vide infra.* L. Bémelmans found that molten **alkali chlorides** react with sulphur, forming, at a high enough temp., sulphur chloride and alkali sulphide, and at a lower temp., sulphide and chlorine. W. Selezneff observed that boiling soln. of the alkali chlorides are not decomposed. A. Manuelli found that a soln. of **cupric chloride** acidified with hydrochloric acid and sulphur heated in a sealed tube at 150°–180°, is partly reduced to a cuprous salt—sulphuric acid is also formed. O. Ruff and H. Golla prepared **aluminium tetrasulphotrichloride,** $AlCl_3.S_4$, by extracting the complex salts of aluminium trichloride and sulphur chloride with carbon disulphide; **aluminium trisulphotrichloride,** $AlCl_3.S_3$, by reducing sulphur chloride with an excess of aluminium; and **aluminium disulphotrichloride,** $AlC_3.S_2$, as in the case of the tetrasulphosalt. M. Raffo and A. Pieroni showed that a colloidal soln. of sulphur reacts with **stannous chloride,** forming stannous sulphide, and hydrogen sulphide. When dehydrated **cupric sulphate** is heated with sulphur, C. Brückner found that it is reduced to cuprous sulphide. G. Vortmann and C. Padberg showed that an excess of hydrochloric acid is necessary for the oxidation of stannous chloride when it is heated with flowers of sulphur. Hydrogen sulphide is formed, and all the tin is converted into stannic chloride. The reaction with **cuprous chloride** is represented: $Cu_2Cl_2+S=CuS+CuCl_2$. W. Wardlaw and F. W. Pinkard obtained a black precipitate containing a large proportion of cuprous sulphide by heating cuprous chloride with finely divided sulphur and dil. hydrochloric acid (112 c.c. of 33 per cent. acid and 138 c.c. of water) at 95° in a current of carbon dioxide. C. F. Rammelsberg, and O. W. Huntington showed that if silver sulphide and cupric chloride act on one another in the presence of air and soln. of sodium chloride, cuprous chloride, silver chloride, and sulphur are produced or the cuprous chloride is converted into a sulphide. They also noted the secondary reaction: $CuS+CuCl_2=Cu_2Cl_2+S$, which is the reverse of G. Vortmann and C. Padberg's reaction. E. Filhol and J. B. Senderens observed no sensible decomposition when a **cupric salt**—sulphate, nitrate, or chloride—is heated with sulphur. W. Wardlaw and F. W. Pinkard represented the reaction which occurs when cupric chloride and sulphur are heated for 4 hrs. with dil. hydrochloric acid (112 c.c. of 33 per cent. and 138 c.c. of water) in a current of carbon dioxide: $6CuCl_2+S+4H_2O=3Cu_2Cl_2+6HCl+H_2SO_4$. In general, colloidal sulphur is much more reactive than other forms of sulphur. According to A. Gerardin, 100 grms. of **stannic chloride** dissolve at

	99°	101°	110°	112°	121°
Sulphur .	5·8	6·2	8·9	9·6	17·0 grms. S.

W. Selezneff observed that the **alkali nitrates** are not decomposed when boiled with sulphur; **alkali sulphates** were also said to resist attack; but J. B. Senderens, observed that the alkali sulphates are slowly decomposed. K. Brückner found that the sulphates of lithium, sodium, and potassium react at a red-heat with the evolution of sulphur dioxide, and the formation of an alkaline residue of sulphide, thiosulphate, and polysulphide. The **alkaline earth sulphates** yield similar products, but react less readily. There is no reaction with **beryllium, magnesium, or aluminium sulphates** at a red-heat. The **sulphates of copper, silver, zinc, cadmium, mercury, thallium, lead, iron** (-ous and -ic), **cobalt, and nickel** are converted into sulphates with the evolution of sulphur dioxide. M. Raffo and A. Pieroni represented the reaction with silver sulphate and a colloidal soln. of sulphur by $3Ag_2SO_4+4H_2O+4S=4H_2SO_4+3Ag_2S$. K. Brückner found that **antimony and bismuth sulphates** yield bluish-grey sulphides of metallic appearance, but in the case of bismuth, the metal is obtained when a smaller proportion of sulphur is employed; **chromic sulphate** yields a black sulphide insoluble in hot hydrochloric acid; **potassium chrome-alum** forms with a prolonged heating chromic oxide and potassium sulphate only, but if the heating is limited, these are accompanied by a compound of potassium and chromium sulphides which is insoluble in water and decomposed by hydrochloric or nitric acid; W. Wardlaw and N. D. Sylvester found that the green soln. of a tervalent **molybdenum salt** reacts with sulphur, forming hydrogen sulphide; quadrivalent molybdenum salts are not reactive with sulphur. According to C. Brückner, a mixture of sulphur and **uranyl sulphate** yields a mixture of uranous and uranosic oxides; and **cerium sulphate** yields a reddish-brown sulphide decomposed by hydrochloric acid. G. N. Lewis and co-workers found that sulphates are not reduced when aq. soln. and sulphur are heated to 150°–180°. W. Selezneff found that the salts of the heavy metals are partly decomposed. G. N. Lewis and co-workers found that nitrates are reduced to nitric oxide when the aq. soln. is heated to 150°–180° with sulphur. E. Filhol and J. B. Senderens said that **copper salts** are not decomposed; lead sulphate is slowly attacked; insoluble **silver salts** are generally blackened, while silver nitrate forms silver sulphide. G. N. Lewis and co-workers found that when aq. soln. of **cupric, mercurous, bismuth, and lead salts** are heated with sulphur to 150°–180°, they are slowly but quantitatively reduced; and **mercuric, ferric, and stannic salts** also are quantitatively reduced. C. Geitner, and E. Filhol and J. B. Senderens made some observations on this subject. G. Vortmann and C. Padberg found that the salts of the -ic oxysalts are more readily attacked than the ous oxysalts; aq. soln. of **zinc, cadmium, manganese, ferrous, and nickel salts,** and **bismuth chloride** are not altered when boiled with sulphur. W. Wardlaw and F. H. Clews found that ferric chloride, in a conc. soln. of hydrochloric acid, is reduced to a small extent by sulphur. W. Selezneff showed that **alkali carbonates** furnish polysulphide, thiosulphate, and carbon dioxide; when heated in sealed tubes, the reaction is reversible—*vide* **2.** 20, 21. The alkaline earth carbonates slowly form thiosulphates; while the metal carbonates react like the corresponding oxides. J. J. Pohl found that a 5·6 per cent. soln. of sodium carbonate dissolves no sulphur at 20°, and about 0·06775 per cent. at 100°. A. Girard observed that **sodium pyrophosphate** is slowly reduced when the aq. soln. is boiled with flowers of sulphur, forming hydrogen sulphide, sodium orthophosphate, and thiosulphate, while T. Salzer represented the reaction: $nNa_4P_2O_7+12S+3H_2O=2Na_2S_5+Na_2S_2O_3+6Na_3HP_2O_7+(n-6)Na_4P_2O_7$; and $Na_2S_5+3H_2O=Na_2S_2O_3+3H_2S$. A little thiophosphate is also formed. J. B. Senderens observed that **calcium and barium phosphates** are slowly decomposed when boiled with water and sulphur; **silver and copper phosphates** are completely decomposed to sulphide, etc.; while **lead, cobalt, and nickel phosphates** are not changed. Arsenates behave in an analogous way: **sodium arsenates** form sulphoarsenates; **silver and copper arsenates** are completely decomposed; lead and nickel arsenates are not decomposed; **sodium arsenite** is decomposed into polysulphide and hydrogen sulphide which forms arsenic trisulphide and finally sodium sulpharsenite. Sulphur reduces boiling **potassium chromate solution;** hydrogen sulphide is given off, chromium sesquioxide is precipitated, and potassium thiosulphate is formed. A soln. of **potassium dichromate** affords, in like manner, chromium chromate with potassium sulphite and sulphate; argentic and mercuric chromates are also attacked, but the lead salt is unaffected. W. Selezneff, J. L. Lassaigne, and O. Döpping also noticed that the **chromates** are decomposed by boiling water and sulphur; while A. Manuelli found that a soln. of potassium dichromate and sulphur, in a sealed tube at 150°–180°, is reduced to chromic oxide—sulphuric acid is also formed. G. N. Lewis and co-workers, and J. B. Senderens showed that **borates** are decomposed when boiled with water and sulphur. J. Hoffmann discussed the blue colour obtained with fused borax, or **boric oxide.** P. Ebell found that sulphur added to molten **glass** gives a yellow or brown-coloured glass. The black colour produced in glass is not, as E. M. Péligot supposed, due to a black allotropic form of sulphur, but, as W. Selezneff showed, it is produced by ferrous sulphide. According to J. B. Senderens, sulphur decomposes boiling soln. of **sodium and calcium silicates** with formation of polysulphides, of some thiosulphate, and evolution of hydrogen sulphide, while sulphur, boiled with powdered glass, determines a similar reaction which is prevented by a previous addition of hydrochloric acid. P. Fenaroli said that the colours produced by sulphur in glass can be interpreted in terms of the varying dispersity of the element. In the case of sulphur, the coloration is due to molecular dispersed sulphur present in the form of polysulphides, and there is no evidence of the presence of colloidal sulphur in glasses of this type.

The physiological action of sulphur.—Sulphur has no action on the skin, but some of it may be converted into hydrogen sulphide which acts as a mild vascular stimulant and with some persons produces eczema; some sulphur may be converted into sulphurous and sulphuric acid which act as irritants. If taken internally, most of it passes out in the fæces unaltered; but a small proportion is converted in the intestine into hydrogen sulphide and other sulphides. These have a mild laxative effect, which is sometimes accompanied by a flatus of hydrogen sulphide which makes sulphur an undesirable laxative. Excessive amounts of sulphides and hydrogen sulphide may produce symptoms of asphyxia, and paralyze the nervous and muscular systems. According to T. Frankl,[6] some sulphur is oxidized to sulphurous acid in the intestine, and if in sufficient amount it may produce hyperæmia, and an increased peristalsis. When sulphur is taken internally, some hydrogen sulphide may be eliminated through the kidneys, the milk, the lungs, and skin; and some is excreted as sulphates in the urine. The breath may smell of it, and silver ornaments near the skin may be discoloured. According to L. C. Maillard, colloidal sulphur, prepared by the interaction of hydrogen sulphide and sulphur dioxide, is completely and rapidly absorbed by rabbits when introduced into the œsophagus. Within twenty-four hours, somewhat less than half is eliminated with the urine as mineral sulphates, and a portion in the form of organic sulphates. The normal amount of the latter is increased by 5–13 per cent. after the ingestion of sulphur, but the proportion falls below normal when this is withdrawn from the diet. About half of the sulphur is excreted in an incompletely oxidized condition, probably in organic combination, since no sulphur, hydrogen sulphide, or sulphur dioxide is formed on treating the urine with acid. It may be supposed that substances are formed by the conjugation of compounds of the type $R.SO_2.OH$ with phenols, and that more highly oxidized compounds escape combination in this way. L. Sabbatani showed that when the hydrosol is injected subcutaneously, hydrogen sulphide is formed only very slowly. After interperitoneal injection it is formed more rapidly, but yet not sufficiently quickly for it to be detectable in the expired air. When injected intravenously, it is readily formed, and for this reason the hydrosol of sulphur is very toxic. As the sulphur aggregates become larger, the toxicity diminishes. The dog can tolerate relatively large doses when the sulphur is introduced into the stomach. With the larger doses vomiting occurs, and the animal rapidly recovers. The sulphur is more toxic under the same condition in rabbits, as these animals cannot vomit. A little more than 0·1 grm. per kilo. of body-weight can produce death. This dose can be well tolerated when introduced intraperitoneally or subcutaneously, although larger doses can act toxically. When given intravenously, doses of 0·0065–0·0203 grm. are toxic, the toxicity depending on the rate at which the sulphur is introduced. E. Salkowsky studied the effect of cabbage on the sulphur compounds in the urine of man and animals. S. Beck and H. Benedict found the excretion of sulphur is increased by muscular work, and when the work has ceased, this is followed by a corresponding decrease. The increase falls specially on oxidized sulphur; the non-oxidized sulphur due to proteid metabolism may be lessened. W. J. Smith said that the union of sulphur and carbon is so strong in some organic substances, that the chemical reactions accomplished cannot sever these elements—*e.g.* acetone-ethylmercaptol, thiophene, and ethyl sulphide. In these three cases the sulphur is combined as $\equiv$C.S.C$\equiv$. The administration of carbamino-thioglycollic acid does augment the urinary sulphates. The same subject was studied by E. Petry. W. J. S. Jerome studied the sulphur excretion in a dog under various conditions; and W. Freund, in infants. The removal of the liver from birds showed that the liver plays no part in the formation of sulphuric acid from the sulphur of food. M. Kahn and F. G. Goodridge have reviewed the whole subject in their *Sulfur Metabolism* (Philadelphia, 1926).

The toxic action of sulphur on the fungus *oidium Tuckeri*, which causes the grape disease, was attributed by R. Marcille [7] to the adherent sulphurous and sulphuric acids. H. J. Waterman found that sulphur inhibits spore formation in the mould *aspergillus niger*. During growth, sulphur accumulates in the cells. According to R. C. Williams and H. C. Young, tests made with sulphurous, sulphuric, and pentathionic acids—all found in water in which sulphur has been triturated—on the spores of the *Sclerotinia cinerea* show that by far the most toxic are the polythionic acids. Although the acidity of the sulphur filtrates is due mainly to sulphuric acid, yet a soln. of this acid of eq. conc. is not toxic. If commercial sulphur is freed from its polythionic acids by suitable treatment with ammonia or nitric acid, it loses its toxicity, but regains it on exposure to air and water. Artificially oxidized sulphurs are also very effective provided the oxidizing agent does not destroy the polythionic acids. Since the polythionate ion is not toxic in neutral or alkaline soln., the toxicity of lime-sulphur sprays is probably dependent on the development of acidity, to liberate the polythionic acid, by weathering of the sulphur.

Over 100,000 tons of sulphur are used per annum in Europe alone for dusting vines and hops. Many experiments have been made to find if sulphur has a beneficial influence as a fertilizing agent. E. B. Hart and W. H. Peterson showed that considerable quantities of sulphur are removed from the soil by common crops. Although the loss is partly compensated by the supply of sulphur from the atm., the latter is probably counterbalanced by the losses the land sustains by drainage. Soils which had been cropped for fifty to sixty years, and had received little or no manure, were found to have lost an average of 40 per cent. of the sulphur trioxide originally present, as determined by comparison with virgin soils, but in cases in which the farm manure had been regularly and liberally applied, the sulphur content of the soil had been maintained or even increased. It is therefore necessary to supply sulphur to the soil in order to replace that removed by the crops and drainage. E. Boullanger found that flowers of sulphur in soil increased the yield from such plants as carrots, haricots, potatoes, etc.; and E. Boullanger and M. Dugardin attributed the favourable influence of small doses of sulphur to its activating effect on bacteria which break down nitrogenous matter in soil to ammonia, and on the nitrification filaments. O. M. Shedd found sulphur increased the production of some crops; it acted injuriously on some; but it had no effect on others. T. Pfeiffer and E. Blanck found that with oats, the addition of sulphur had a slightly depressing effect, and it did not increase the yield or utilization of nitrogen. J. A. Voelcker observed no effect with mustard, rape, and clover. W. Pitz obtained a slightly increased yield of red clover without influencing the development of the roots or root nodules. A. R. Thompson studied the effect on the rice plant. W. Pitz observed that 0·05 per cent. of sulphur decreased the number of bacteria on agar-agar plates; there was an increased production of ammonia, and a decreased yield of nitrates. J. R. Neller found that legumes show an increase in their nitrogen constant when grown in soils containing sulphur; non-legumes do not seem to be affected in any way by the sulphur. Sulphur is not so likely to prove advantageous on acidic soils, and on those soils which are improved by marling. H. C. Lint observed the acidity of soils increased gradually after the addition of sulphur. The sulphur is oxidized more rapidly in heavy clay loam soils than in sandy loam soils—*vide supra.* C. Brioux and M. Guerbet stated that the oxidation of sulphur in soils is entirely due to bacterial action. G. Bosinelli observed an insignificant increase in the conversion of organic nitrogen compound in soils into ammonia. According to W. Thörner, the oxidation products of the sulphur compounds in peat are injurious to plants, and also to mortars and cements. A. Hotinger discussed the rôle of sulphur and sulphides in biological oxidations and reductions. The oxidation of sulphur in soils by sulphur bacteria was studied by J. G. Lipman and co-workers—*vide supra* for sulphur bacteria. F. F. Nord investigated the effect of heat and $H^{\cdot}$-ion conc. on the biological transportation system containing sulphur.

The uses of sulphur.[8]—Sulphur is employed in the preparation of numerous sulphur compounds, and preparations—*e.g.* sulphuric acid, ultramarine, vermilion, and sulphur dioxide for making the *bisulphite of lime*—*i.e.* calcium hydrosulphite—used in the wood-pulp industry. It is used in the preparation of gunpowder, matches; and in vulcanizing rubber.[9] It is employed as a fungicide in combating the so-called grape-disease,[10] etc.; as a disinfectant—*vide infra,* sulphur dioxide; in certain pharmaceutical preparations; and as a parasiticide for the *Sarcoptes hominis.* The so-called *sulfozon* is powdered sulphur with much adsorbed sulphur dioxide.[11] The insulating qualities of sulphur have some applications; and in consequence of its inertness towards many chemical agents, it is employed as a cement either alone or in admixture with sand—*e.g.* in setting the brick-linings of acid-towers; in constructing storage-tanks; paving-floors; in the luting of jars, etc. For this purpose, the sulphur is melted. If not well stirred, the sulphur may become viscous and take fire if in the open air. It may be fused in jacketed-pans heated by steam at, say, 30 lb. press. J. Myers [12] used sulphur for the drying of gases. It is also used as a "fixed point" in graduating pyrometers; and for high temp. vapour-baths in the laboratory. Sulphur is used in taking casts of various objects. According to C. Lepierre,[13] if molten sulphur at 115° be poured on printed or written paper, on cooling it acquires a sharp impression of the characters, W. H. Kobbé [14] described the indurating of wood with sulphur to preserve, harden, and strengthen it, and make it more acid-resisting. The impregnation of concrete with molten sulphur has also been recommended for electrolytic cells, etc., to make it stronger and impervious to acids.

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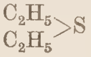
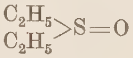
§ 8. The Valency and Atomic Weight of Sulphur

The **valency** of sulphur is variable. Formerly, when the theory of constant valency was fashionable, it was supposed that sulphur was bivalent, and compounds like SO_2 and SO_3 were symbolized by closed chain formulæ, and sulphuric acid, H_2SO_4, was represented HO.S.O.O.OH. Actually, sulphur appears to be bivalent towards hydrogen ; quadrivalent and sexivalent towards oxygen ; and sexivalent towards fluorine—H. Moissan and P. Lebeau's[1] SF_6. A. A. Blanchard, and A. P. Mathews made some speculations on this subject. The variable valency of sulphur is illustrated by ethyl sulphide, and its oxidation products—ethyl sulphoxide, and ethyl sulphone—described by A. von Oefele :



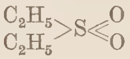
$$\begin{array}{l}C_2H_5\\C_2H_5\end{array}\!>\!S$$

Ethyl sulphide



$$\begin{array}{l}C_2H_5\\C_2H_5\end{array}\!>\!S{=}O$$

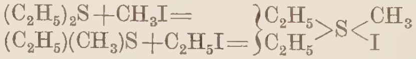
Ethyl sulphoxide



$$\begin{array}{l}C_2H_5\\C_2H_5\end{array}\!>\!S\!\ll\!\begin{array}{l}O\\O\end{array}$$

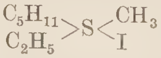
Ethyl sulphone

H. C. Klinger and A. Maassen showed that the same products are obtained when ethyl sulphide is treated with methyl iodide, as when methylethyl sulphide is treated with ethyl iodide :



$$\begin{array}{l}(C_2H_5)_2S+CH_3I=\\(C_2H_5)(CH_3)S+C_2H_5I=\end{array}\Big\}\begin{array}{l}C_2H_5\\C_2H_5\end{array}\!>\!S\!<\!\begin{array}{l}CH_3\\I\end{array}$$

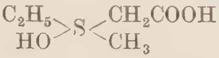
Hence, unless an intramolecular change to a more stable condition takes place during the formation of the methyldiethylsulphonium iodide, the three valencies to which the alkyl-groups are attached must be equivalent. The different results obtained by F. Krüger, and J. A. Blaikie and A. C. Brown, were ascribed by H. C. Klinger and A. Maassen to the presence of impurities. R. Nasini and A. Scala supported the view that the products are different because the products furnish complex salts with platinum tetrachloride, one forming cubic and the other monoclinic crystals. The different ways of preparing methylethylamylsulphonium iodide :



$$\begin{array}{l}C_5H_{11}\\C_2H_5\end{array}\!>\!S\!<\!\begin{array}{l}CH_3\\I\end{array}$$

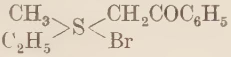
described by A. Brjuchonenko, supported the conclusion of H. C. Klinger and A. Maassen. The quadrivalency of sulphur is emphasized by the existence of sulphur tetrachloride ; by the formation of thionyl chloride, $SOCl_2$, from sulphur tetrachloride and trioxide, observed by A. Michaelis and O. Schifferdecker ;

and by the existence of compounds of the type $MS(C_2H_5)_2Cl$, observed by C. W. Blomstrand. R. De supposed that the three alkyl groups in the sulphonium compounds are held by tervalent sulphur, and that the halogen is attacked by an electrostatic bond. W. J. Pope and co-workers concluded from the non-activity of the thetine salts, also studied by L. Vanzetti:

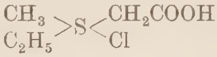


$$\begin{matrix}C_2H_5\\HO\end{matrix}\!>\!S\!<\!\begin{matrix}CH_2COOH\\CH_3\end{matrix}$$

that the four groups directly united to the sulphur atom lie in the same plane; but this hypothesis was not confirmed by the later work of W. J. Pope and S. J. Peachey, D. Strömholm, and S. Smiles, who were able to prepare optically active compounds containing an asymmetric sulphur atom; thus,

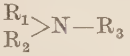


$$\begin{matrix}CH_3\\C_2H_5\end{matrix}\!>\!S\!<\!\begin{matrix}CH_2COC_6H_5\\Br\end{matrix}$$



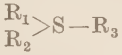
$$\begin{matrix}CH_3\\C_2H_5\end{matrix}\!>\!S\!<\!\begin{matrix}CH_2COOH\\Cl\end{matrix}$$

This subject was discussed by M. Scholtz, and R. F. Goldstein. The optical activity persists when these compounds are dissolved in water, and ionization has occurred. Hence, added T. M. Lowry, optical activity occurs in a trisubstituted sulphonium ion, although it does not exist in the analogous molecule of ammonia:



$$\begin{matrix}R_1\\R_2\end{matrix}\!>\!N-R_3$$

Inactive

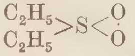


$$\begin{matrix}R_1\\R_2\end{matrix}\!>\!S-R_3$$

Active

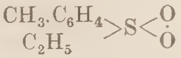
He continued: no analogous difference exists between the electronic formula for the two groups since in each case the central atom carries three pairs of shared electrons, with one " lone pair " to complete the octet. The contrast is, therefore, probably due to the existence in the nitrogen-compound of a mobility of atomic or molecular structure, similar to that which makes it easy to form a double or triple bond between elements of the first short period, whereas this is difficult or impossible in elements of the later periods.

E. Divers tried to show that the sulphites contain only a quadrivalent sulphur atom—*vide infra*; and A. Michel and A. Adair said that the sulphones may be similarly regarded as compounds with a quadrivalent sulphur atom, *e.g.*:



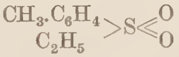
$$\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!>\!S\!<\!\begin{matrix}O\\O\end{matrix}$$

According to R. Otto and A. Rössing, the sulphinic acids may be regarded as compounds of either quadrivalent or sexivalent sulphur:



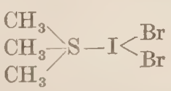
$$\begin{matrix}CH_3.C_6H_4\\C_2H_5\end{matrix}\!>\!S\!<\!\begin{matrix}O\\O\end{matrix}$$

or



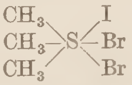
$$\begin{matrix}CH_3.C_6H_4\\C_2H_5\end{matrix}\!>\!S\!\ll\!\begin{matrix}O\\O\end{matrix}$$

R. C. Casanova argued in favour of the sexivalency of sulphur. L. Dobbin and D. O. Masson prepared compounds of the type illustrated by $(CH_3)_3SIBr_2$, which may be represented with either a quadrivalent or a sexivalent sulphur atom:



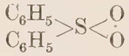
$$\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\!>\!S-I\!<\!\begin{matrix}Br\\Br\end{matrix}$$

or



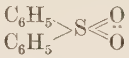
$$\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\!>\!S\!<\!\begin{matrix}I\\Br\\Br\end{matrix}$$

but they favoured the latter hypothesis. E. A. Werner prepared a tetrachlorotrimethylsulphonium iodide, $(CH_3)_3SClICl_3$, which was not considered to favour the assumption of an octovalent sulphur, but rather a sexivalent sulphur atom with halogens having a higher valency than unity. The sexivalency of sulphur was also discussed by T. P. Hilditch and S. Smiles, W. J. Pope and H. A. D. Neville, J. A. N. Friend, etc. R. H. Pickard and J. Kenyon, and R. Hermann prepared additive compounds with the sulphoxides of the type $(C_6H_5)_3SO$, but not additive compounds with the sulphones of the type $(C_6H_5)_2SO_2$. They therefore assume that the sulphones have a ring structure in which the residual valencies are mutually satisfied :



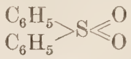
$$\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\!>\!S\!<\!\begin{matrix}O\\\cdot\\O\end{matrix}$$

or



$$\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\!>\!S\!\ll\!\begin{matrix}O\\:\\O\end{matrix}$$

and not



$$\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\!>\!S\!\ll\!\begin{matrix}O\\O\end{matrix}$$

For the grouping of the sulphur atoms in the molecule, *vide supra*, blue colloidal sulphur ; and for the molecular weight of sulphur, *vide supra*, physical properties of sulphur. J. Piccard and J. H. Dardel, and V. M. Goldschmidt discussed the valency of sulphur from the point of view of the co-ordination theory.

In 1808, J. Dalton [2] made an estimate of the **atomic weight** of sulphur. He said :

> I deduce the weight of an atom of sulphur to be nearly 14 times that of hydrogen ; it is possible that it may be somewhat more or less, but I think that the error cannot exceed 2.

J. J. Berzelius' early values for the at. wt. of sulphur were equally faulty ; later he made observations on the synthesis of lead sulphate and obtained 32·12 for the at. wt. of sulphur. He also obtained $AgCl : Ag_2S=100 : 86·4737$ for the ratio of silver chloride to silver sulphide formed by heating the chloride in hydrogen sulphide, while L. F. Svanberg and H. Struve obtained 86·472. O. L. Erdmann and R. F. Marchand determined the amount of calcium sulphate which could be obtained from calcium carbonate ; and fixed the value for sulphur by reference to calcium and to mercury. They thus obtained 32·011 for the at. wt. of sulphur. J. B. A. Dumas heated silver in the vapour of sulphur and obtained for the ratio $Ag : Ag_2S=100 : 114·8234$; and J. S. Stas obtained 100 : 114·8522. J. P. Cooke reduced silver sulphide in hydrogen at a temp. low enough to hinder the volatilization of silver, and he obtained the ratio 100 : 114·888, and 100 : 114·8165. H. Struve determined the ratio of silver to silver sulphate, and found $Ag : AgSO_4=69·230 : 100$; while J. S. Stas obtained 69·203 : 100. T. W. Richards converted sodium carbonate into sodium sulphate, and obtained for the ratio $Na_2CO_3 : Na_2SO_4=100 : 133·985$; while T. W. Richards and C. R. Hoover gave 32·062 when the value for sodium is 22·995. T. W. Richards and G. Jones converted silver sulphate into the chloride by heating it in a stream of hydrogen chloride and obtained $Ag_2SO_4 : AgCl =100 : 91·933$. F. B. Burt and F. L. Usher calculated 32·067 from the ratio of nitrogen to sulphur in the decomposition of nitrogen sulphide (at. wt. N=14·009). In agreement with his bias in favour of the " whole number " theory of at. wts., G. D. Hinrichs gave 32 for the at. wt. of sulphur. J. D. van der Plaats calculated 32·059 from J. S. Stas' data, and J. Thomsen, 32·074. F. W. Clarke's summary of the data available up to 1910 gave 32·0667. E. Moles, and P. A. Guye said the best representative value of the experimental work lies between 32·048 and 32·056. The International Table for 1926 gives 32·06.

Attempts have been made to calculate the at. wt. of sulphur from physical data. A. Leduc obtained from the densities of sulphur dioxide and hydrogen sulphide, the value S=32·056 ; and from the method of limiting densities, D. Berthelot obtained S=32·050 ; and R. Wourtzel, 32·059. A. Jaquerod and A. Pintza obtained 32·01 for the at. wt. of sulphur calculated from density determinations of sulphur dioxide ; A. Jaquerod and O. Scheuer, 32·036 ; and G. Baume, 31·952. P. A. Guye calculated from the critical constants of sulphur dioxide, 32·065 ; G. Baume and F. L. Perrot, 32·070 from the vap. density of hydrogen sulphide ; and G. M. Maverick, 32·100 from compressibility data.

The **atomic number** of sulphur is 16. F. W. Aston's [3] positive ray analysis indicated that in addition to the primary atoms of mass 32 there are **isotopes** of mass 33 and 34 amounting to above 3 per cent. of the whole ; the S_{34} atoms appear to be about 3 times as abundant as the S_{33} atoms. E. Rutherford and J. Chadwick observed no signs of **atomic disintegration** when sulphur is bombarded by α-particles, but H. Pettersson and G. Kirsch observed that the atom can be disrupted by bombardment with α-rays. The subject was discussed by G. I. Podrowsky. N. Bohr represented the **electronic structure** : (2) (4, 4) (4, 2). H. G. Grimm and A. Sommerfeld, D. R. Hartree, C. D. Niven, A. M. Taylor and E. K. Rideal, S. C. Biswas, R. H. Ghosh, W. Kistiakowsky, J. K. Syrkin, W. Krings, T. M. Lowry, M. L. Huggins, C. G. Bedreag, F. Hand, W. Pauli, and C. P. Smyth, made observations on the electronic structure of sulphur, and H. Burgarth, and H. Collins have made some speculations on the subject.

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§ 9. Hydrogen Sulphide

This fœtid-smelling gas was not described by the ancient Greek writers although it is frequently found issuing from springs and craters on the northern shores of the Mediterranean Sea. It is related that Pythia, the oracle of Apollo, in the temple at Delphi, was thrown into an ecstatic frenzy by inhaling some peculiar vapour ascending from a chasm in the ground of the ἄδυτον of the temple. The priestess then spoke—often with shrieks and ravings—the answers of the invisible god Apollo. It has been suggested that the vapour which issued into the adytum was hydrogen sulphide gas; but this is a fanciful hypothesis because, although the gas does excite the senses, there is no real evidence to enable the chemist to identify the atmosphere in the adytum with the malodorous hydrogen sulphide.[1]

In the *Collection des anciens alchimistes grecs*, by M. Berthelot and C. E. Ruelle (Paris, 1887), it is stated that No. X of the Leyden papyri contains a description of different forms of ὕδωρ θεῖον, *the water of sulphur*, or, by a play on the double meaning of the word θεῖον, *the divine water*. The mode of preparation indicates that the liquid was a polysulphide of calcium which could give black, yellow, or red precipitates, and colour the surface of metals. There is here no indication of the power subsequently attributed to the divine water of transmuting metals into gold. In the apocryphal *Physica et mystica*, ascribed to Democritus of Abdera, however, the divine water is employed to obtain gold, for it says that when *androdamus* (arsenic sulphide) is mingled with brine and antimony; calcined until it becomes yellow, and boiled in the water of sulphur, it will produce, when thrown upon silver, χρυσοζώμιον—*i.e.* juice of or tincture of gold. M. Berthelot and C. E. Ruelle noted that this simply means that silver will be superficially tinted like gold. The third-century writer, Zosimus of Panopolis, the first alchemist of known date—**1**. 1, 11—called water of sulphur "the great mystery." He said that this water, like a leaven, changes to its resemblance substances with which it is treated. The leaven was supposed to contain the distinctive qualities of gold, and to cause the molten metal on which it was thrown to ferment, changing it thereby into its own nature. This seems to be the first expressed definition of the philosopher's stone, and the theory was accepted by the alchemists of the Middle Ages as the action which takes place in the process of transmutation.[2] Zosimus frequently alluded to the unpleasant smell of the divine water, but not until the sixteenth century has any further mention of this smell been found to occur in the literature of alchemy.

In 1595, A. Libavius[3] alluded to the blackening of ceruse by the fumes of sulphur; in 1664, R. Boyle, to the blackening of silver by the fumes from liver of sulphur; in 1675, N. Lemery, to the blackening of silver by the vapours of sulphur emitted during the preparation of milk of sulphur; and in 1722, F. Hoffmann referred to the smell, like rotten eggs, which is emitted during preparation of the *lac sulphuris*. F. Meyer, in 1764, described the combustibility of the aeriform fluid emitted when *hepar sulphuris* is treated with acids; and H. M. Rouelle, in 1774, observed that the aq. soln. has the same odour as the gas, and deposits sulphur when it is kept some time. He also showed that the gases from the liver of sulphur, and from sulphuretted mineral waters, are the same. C. W. Scheele, in 1777, reported that the gas can be obtained by the action of acids on liver of sulphur prepared with alkali or lime, or on manganese or iron sulphide; and by heating sulphur in hydrogen. He found that the gas gives sulphur when treated with nitric acid or with chlorine, and inferred that it contained sulphur, phlogiston, and caloric. F. Meyer had previously stated that the contained sulphur makes the gas inflammable. A. Baumé also supposed that the gas contains sulphur and phlogiston. Immediately after C. W. Scheele, T. Bergman proved that the sulphurous properties of many mineral waters depend on the presence of this gas; and he mentioned that the gas reddens litmus paper, and showed that it reacts with soln. of numerous salts of the metals. The gas was now investigated by many chemists, P. Gengembre, J. Senebier, etc. L. Viellard found indications of this gas in putrid blood. R. Kirwan called the gas *hepatic air*, and stated that it occurs in coal-pits, and that it is the peculiar product of the putrefaction of many animal substances; and "rotten eggs and corrupt water are known to emit the smell peculiar to this species of air, and to discolour metallic substances in the same manner." R. Kirwan examined the action of the gas on soln. of the salts of the metals, and emphasized the acidic nature of the gas. He thought that the gas contained no hydrogen, and said that "it is difficult to conclude that hepatic air consists of anything else than sulphur itself, kept in an aerial state by the matter of heat." C. W. Scheele called the gas *die stinkende Schwefelluft;* it was also called *Schwefelleberluft;* A. N. Scherer, and L. W. Gilbert gave it the name *Schwefelwassergas;* and J. B. Trommsdorff, *Hydrothionsaure.* A. F. de Fourcroy, and C. F. S. Hahnemann employed the gas in the detection of lead in wines. The gas was analyzed by A. B. Berthollet in 1796, and shown to be *hydrogène sulfuré*—hydrogen sulphide or *sulphuretted hydrogen.*

The occurrence of hydrogen sulphide.—Hydrogen sulphide is found in the air of sewers and cesspools; it occurs in the emanations from moist earth or moist slag containing pyrities or metal sulphides. It is formed whenever albuminous matter putrefies—*e.g.* eggs, the corpses of man or animals. It is found in the air of towns, and it then causes the blackening of silver ornaments not kept bright by repeated use—*vide* atmospheric air, **8.** 49, 1. The gas is given off along with other gases from numerous springs. The offensive smell of mineral waters of Harrogate is usually due to the presence of dissolved hydrogen sulphide. As E. Goldschmidt[4] has said, many of the so-called *sulphur springs* are known—as, for instance, at Niagara Falls, the Yellowstone National Park, Wyoming, the Stinkwater River, and the Red Sulphur Springs of Sharon—where hydrogen sulphide is said to be exhaled to the disgust of those who live in the neighbourhood. According to J. F. Daniell, and B. Lewy, sea-water contains some hydrogen sulphide; R. C. Miller and co-workers found it in the water of San Francisco Bay; B. Lewy said that 300 parts of the sea-water off Caen contained one part of the gas. A. Archangelsky discussed the formation of hydrogen sulphide in the mud of the Black Sea. E. V. Smith and T. G. Thompson observed that on the Lake Washington Ship Canal, hydrogen sulphide is produced by bacteria acting on the sulphates contained in the stagnant or sluggish brackish waters; and the elimination of most of the oxygen from the water precedes the appearance of hydrogen sulphide. M. Yegunoff said that diffusion experiments with the waters of the Black Sea discredit the view that hydrogen sulphide is formed at the sea-bottom and diffuses upwards. It is probably formed throughout the whole thickness of the water, and accumulates at the bottom where it cannot be oxidized. This subject has been discussed previously in connection with the occurrence of sulphur. E. S. Bastin and co-workers discussed the sulphate reducing bacteria of the oil-wells of Illinois, and California. The following sulphur springs, amongst others, have been reported:

J. von Liebig described the sulphur springs at Aachen; E. Willm, Aix-les-Bains (Savoy); E. Ludwig and T. Panzer, Altenburg; A. P. Poggiale, Amélie-les-Bains; C. Schmidt, Arasau (near Kopal); L. Waagen, Baden; W. von Filhol, C. Moureau and A. Lepape, and F. Garrigou, Bagnières de Luchon (Pyrenees); P. F. G. Boullay and O. Henry, Barèges and Barzun (Pyrenees); E. Willm at Olette, Pyrénées Orientales; C. Schmidt, Belucha near Altai (Siberia); J. L. Smith, at Boll Bruna (Asia Minor); R. Wildenstein, Burtscheider Quelle; A. and G. Negri, Casteggio (Cremona); L. Burgerstein, Cantets (Altenburg); L. Marton, Eaux-Bonnes (Pyrenees); A. Schoof, and C. R. Fresenius, Eilsen; A. Bechamp, Fumades (d'Alais); L. R. von Fellenberg Grosswardein, Gurnigel-Bad (Bern); T. E. Thorpe, R. H. Davis, W. A. Hofmann, S. Muspratt, T. Fairley, P. A. E. Richards, C. H. Bothamley, A. E. Wilson and H. Ingle, and C. L. Kennedy and M. N. Johnstone, Harrogate; R. von Drasche, Japan; B. von Lengyel, Hechingen (Kolop); G. Massol, and P. Besson, Isère-les Bains; H. von Meyer, Landeck; R. Bunsen, and F. Wandesleben, Langenbrücken (Baden); E. Sarasin, C. E. Guye and J. Micheli, Lavey (Switzerland); J. C. Wittstein, Le Prese (Craubunden); S. Brigel, and P. Balley and S. Brigel, Lostrof (Solothurn); M. Gossart, Muerchin (Pas-do-Calais); C. Schmidt, Monbarry; O. Henry, Montbrun (Dept. de Dôme); L. de Marchi, Montegrotto (Euganei); E. Witting, Nenndorf (Lippspringe); C. R. Fresenius, Neudorf; L. A. Buchner, Oberdorf (Algäu); E. Willm, Olette

(Pyrenees); F. Wandesleben, Oestringen (Baden); A. Casselmann, Porchow near Chilowo; F. von Bibra, Pystian (Rothenburg); G. Bizio, Reutlingen (San Daniele, Venedig); C. von Hauer, San Stefano; L. Dieulafait, P. Bolley and W. Schweitzer, and A. Hartmann, Schinznach (Aargan); F. Henrich and G. Prell, Luisenburg (Fichtelgebirge); E. Müller, Sebastrianweiler (Seebruch); E. Egger, Seon (Oberbayern); C. Schmidt, Smorgon (Russia); A. Theegarten, Sophia; A. Vierthaler, Spalato; T. Simmler, Stackelberg (Glarus); R. Nasini and C. Porlezza, and D. Vitali, Tabiano-Salzomaggiore; E. E. Lang, and F. C. Schneider, Trentschin (Töplitz); A. Albertoni, F. Lussana and M. Rota, Trescore; C. Ochsenius, Utah; A. Agrestini, Val de Gallo; A. B. Poggiale, Viterbo; C. von Hauer, Warasdin (Töplitz); and G. F. Walz, Wiesloch (Baden).

The origin of sulphur springs has been discussed by A. Gautier,[5] G. Bischof, E. Planchud, F. Auerbach, O. Hackl, etc. J. Thomann observed that the presence of hydrogen sulphide in bottled mineral waters must be attributed to the presence of micro-organisms. In the water of Passug, there is an anaërobic spirillum which reduces sulphates. According to R. Piria, the hydrogen sulphide from the fumaroles of Agnano (Naples) can be ignited by a piece of lighted tinder. Hydrogen sulphide is a constituent of most of the so-called volcanic gases. This was shown by the analyses of R. W. Bunsen made on the fumaroles, etc., in the neighbourhood of Hekla, Iceland, by C. J. St. C. Deville and F. Leblanc on the volcanic gases of Vesuvius, Vulcano, Etna, and various springs in Sicily; by H. Gorceix, on the gases from Vesuvius, Santorin, and Nisyros; A. Brun, on the exhalations from Vesuvius, Stromboli, the volcanoes of Java, and the Canary Islands, and Kilauea; C. A. Kténas, the exhalations from the Santorin volcano; R. Nasini and co-workers, on the gases from Vesuvius, the Flegrei Plains and the Albule Waters of Tivoli, and the Springs of Viterbo, Pergine, and Salsomaggiore; by F. Fouqué, on the volcanic gases from fumaroles associated with Vulcano, the volcanic eruptions of Santorin, and a submarine eruption near the Azores; by O. Silvestri, S. von Waltershausen and A. von Lasaulx, I. G. Ponte, on the exhalations from Etna; by C. F. X. Rochet d'Héricourt, on the solfatara of Dufane, Abyssinia; by A. von Humboldt, on the solfatara of Urumtsi, Chinese Tartary; by T. Wolf, on the exhalations from Cotopaxi; by H. Moissan, and A. Lacroix, on the emanations from the fumaroles, etc., of Mont Pelée, Martinique; by C. Velain, on the exhalations from St. Paul Island; A. L. Day and E. S. Shepherd, W. Libbey, E. T. Allen, on the gases from Kilauea; E. T. Allen and E. G. Zies, on the gases from Mount Katmai, Alaska, and the fumaroles of the Valley of Ten Thousand Smokes. General observations on the subject were made by E. T. Allen, W. Hempel, A. Brun, E. de Beaumont, and T. Thorkelsson. F. C. Phillips showed that the natural gas escaping from the well at Point Albino, Canada, contains hydrogen sulphide; C. C. Howard, in the natural gas of Indiana and Ohio; and W. H. Cadman, in the natural gas of Persia. P. Pfeiffer[6] found hydrogen sulphide in the gases associated with the Stassfurt salt deposits; A. Gautier, in the occluded gases of granites. R. T. Chamberlain discussed the subject of occluded gases in rocks. Hydrogen sulphide occurs in the so-called stinking limestones discussed by W. Spring, Y. V. Samoiloff and V. A. Zilbermintz, W. Nenadkevitsch, W. Vernadsky, and B. J. Harrington. The liberation of hydrogen sulphide from gob-fires in coal was discussed by T. J. Drakeley. The occurrence of hydrogen sulphide in the stomach was examined by I. Boas, and H. Strauss; in urine, by F. Müller; in boiled milk, by F. Utz; and in sewage, by A. B. Porter and J. A. Cresswick.

The formation and preparation of hydrogen sulphide.—R. Kirwan[7] founded an argument that hydrogen sulphide does not contain hydrogen because "hepatic air could not be procured from the direct union of inflammable air and sulphur." This is all wrong, for C. W. Scheele, and H. Davy showed that when sulphur is heated to a temp. near its b.p. in hydrogen, or when hydrogen is passed over melted sulphur, combination between the two elements occurs slowly and incompletely, so that even after a long period of time, a large proportion of hydrogen remains uncombined; the vol. of the hydrogen is not changed by union with the sulphur. A. Cossa observed that sulphur vapour burns in hydrogen gas. B. Corenwinder passed a mixture of sulphur vapour and hydrogen over pumice-stone at 400°.

D. P. Konowaloff, F. Jones, A. Cossa, R. F. Bacon, and V. Merz and W. Weith obtained confirmatory results; and M. G. Weber obtained 10 per cent. better yields by using pumice-stone as contact catalyst; at 325°, the mixed gas contained 46·1 per cent. of H_2S; at 400°, 58·0 per cent.; and at 475°, 58·9 per cent. I. Taylor obtained impure hydrogen sulphide by passing coal-gas over boiling sulphur. The hydrogen, not the hydrocarbons, of the coal-gas here reacts with the sulphur. P. Hautefeuille heated hydrogen and sulphur in a sealed tube at 440°. On the other hand, J. Myers said that hydrogen sulphide is rapidly decomposed at the b.p. of sulphur.

R. Januario said that the direct union of the two elements begins at 120°, and is quite perceptible at 200°. The reconciliation of these statements turns on the fact, demonstrated by H. Pélabon, that the reaction is reversible, for the combination is not complete between 200° and 350°. M. Cluzel showed that hydrogen sulphide is decomposed into its elements when it is passed through a red-hot tube; J. Myers said that the reaction begins at 400°, and H. Pélabon, that it is quite perceptible at 440°. N. Beketoff observed that at a red-heat about 7 per cent. of the gas is decomposed; and C. Langer and V. Meyer said that decomposition is complete at about 1690°. H. Pélabon found that if p denotes the partial press. of the hydrogen sulphide and P the total press. of the gas, the ratio p/P is 0·0210 at 200°; 0·0541 at 235°; 0·13 at 255°; 0·3355 at 280°–285°; 0·69 at 310°; and 0·972 at 350°. In the case of the gas at 280°–285°, the ratio after 38 hrs.' heating was 0·098; after 162 hrs.', 0·3356; and after 300 hrs.', 0·3354. At this temp., therefore, hydrogen sulphide will be formed in the system containing hydrogen, hydrogen sulphide, and sulphur vapour, in contact with liquid sulphur, so long as the ratio is included between 0 and 0·3355; but the reverse change with hydrogen sulphide does not occur, the ratio remains nearly unity when the temp. is maintained at 280°. Hence, the mixture of hydrogen, hydrogen sulphide, and sulphur vapour, in contact with liquid sulphur, should have a ratio approaching unity if the system is to remain in a true state of equilibrium at this temp.; the fact that the ratio does not exceed 0·3355 is taken by P. Duhem to mean that the equilibrium is only apparent or in a state of what he calls *le faux équilibre*. H. Pélabon showed that when sulphur and hydrogen are heated in sealed tubes, and afterwards cooled, the final composition of the gaseous mixture depends on the mass of sulphur employed, and the proportion of hydrogen sulphide is higher the higher the proportion of sulphur. The composition of the gaseous mixture in the cooled tube corresponds the more nearly with that of the gaseous mixture. When the proportion of the sulphur is low, but yet in excess, combination takes place more quickly the higher the temp., and the maximum quantity of hydrogen sulphide that can be formed increases very regularly with the temp. With larger masses of sulphur, the quantity of hydrogen sulphide dissolved by the fused sulphur increases with the temp. When the hydrogen is mixed with nitrogen, the maximum quantity of hydrogen sulphide formed is less than with pure hydrogen for the same time of heating, but, other conditions being the same, the difference is smaller the higher the temp. M. Bodenstein could not confirm the experimental results on which P. Duhem's theory of false equilibrium is based. He found the reaction to be quite normal between 234° and 356°, and the velocity constant, k,

	234°	283°	310°	356°
k . .	0·0000018	0·0000329	0·000118	0·0028

The reaction is of the first order, and is therefore represented by $H_2+S=H_2S$. When the conc. of the sulphur is varied, the velocity is proportional to the sq. root of the conc., a surprising result in view of the complexity of sulphur mols. It may, however, be explained by the assumption that three actions occur—(i) $S_8 \rightleftharpoons 4S_2$, (ii) $S_2 \rightleftharpoons 2S$, (iii) $H_2+S=H_2S$, and that of these the velocity of (i) is very small, and of (ii) very great compared with (iii). The velocity of (iii) will then be proportional to the sq. root of the concentration of the S_2 mols., and this, owing to the rapid removal of the latter, proportional to the conc. of the S_8 mol. There is nothing improbable in P. Duhem's *les états de faux équilibre,* but H. Pélabon's results with hydrogen sulphide could not be confirmed by R. G. W. Norrish and E. K. Rideal, for they observed no sign of such a state in their observations on the speed of the reaction between sulphur in a current of hydrogen. They assumed that the bulbs in H. Pélabon's experiment were not heated long enough for equilibrium.

R. G. W. Norrish and E. K. Rideal found that combination between hydrogen and sulphur occurs by way of two reactions, a gaseous reaction proportional to the press. of the hydrogen, and a surface reaction independent of the press. of the hydrogen. The temp coeff. is 1·48 for the surface, and 2·19 for the gaseous reaction. The surface reaction is directly proportional to the internal surface of the vessel and is independent of the quantity of sulphur in the bulb. The heats of activation of the gaseous and surface reactions are 52,400 and 26,200 cals., respectively, the former being exactly double the latter. It is suggested in explanation of this that the sulphur molecules can become activated in two stages. The critical increment—*i.e.* the energy necessary for the rupture of the sulphur bonds—is 51,460 cals. at 300° for the gaseous, and 25,750 cals. at 300° for the surface reaction. The critical increment of the surface reaction is taken to correspond with the breaking of one sulphur bond, and to be equal to that energy required to sublime a molecule of S_2 from the surface, which also involves the breaking of one bond. The surface reaction is considered to take place in two stages—(1) adsorption of the molecule, involving breaking of one bond, and (2) removal of the molecule of hydrogen sulphide, involving breaking of the second bond, the critical increment measured corresponding only to the slower of these two processes. By assuming a small percentage of the stable and saturated S_8 mols. of which the surface is mainly composed to be opened by the rupture of one linkage and thus polarized, the adsorption of hydrogen and oxygen and the catalytic action of the latter can be explained. The presence of oxygen acts as a catalytic agent, and as the temp. rises to 265°, that gas retards or poisons the reaction when more than 10 per cent. is present, and at 285° when more than 7 per cent. is present. The phenomenon is complex. There is (i) a strong poisoning effect in the gaseous reaction between hydrogen and sulphur at all temp., and (ii) a catalytic effect on the surface reaction which becomes observable only at low temp. (265° and 285°), where the surface reaction is of greater relative importance. This surface catalytic action rises to a maximum with increase of oxygen conc. in the hydrogen and then falls off, finally becoming a poisoning action for conc. of oxygen beyond 10 per cent. At the same time, sulphur dioxide is formed at a rate directly proportional to the conc. of the oxygen. The effects observed can be quantitatively explained by postulating a gradual preferential adsorption of oxygen by the sulphur surface, all the hydrogen being displaced when the gaseous conc. of oxygen has exceeded 10 per cent., and ascribing to the oxygen a catalytic activity proportional to the number of mols. adsorbed per sq. cm. of surface. H. A. Taylor and C. F. Pickett studied the decomposition of hydrogen sulphide by heated platinum filaments near 1000°, and found that the decomposition curves have two branches showing an increased decomposition as the rate of flow is increased, separated by a region where the amount of decomposition is constant and independent of the rate of flow. This branch decreases as the temp. rises, becoming a point of inflexion at 1269°. There is supposed to be (i) a primary absorption of gas with the sulphur atoms oriented with respect to the platinum; (ii) a splitting of the adsorbed molecule with the escape of hydrogen, and subsequent evaporation of the sulphur.

G. Preuner and W. Schupp studied the reaction with hydrogen and sulphur vapour at a temp. where the molecules of sulphur are diatomic. The following represent the equilibrium constants for pressures, K_p, and for volumes, K_v, where $K_v = K_p/RT$, and $[H_2S] = K[H_2][S_2]^{\frac{1}{2}}$:

	750°	830°	945°	1065°	1132°
$K_p \times 10^4$.	0·89	3·8	24·5	118	260
$K_v \times 10^6$.	1·06	4·2	24·5	107·5	226

M. Randall and F. R. von Bichowsky worked at temp. between 750° and 1394°; the collected results are:

	750°	830°	945°	1065°	1132°	1200°	1364°	1394°
Log K_p .	2·025	1·710	1·305	0·964	0·793	0·643	0·490	0·257

Observations were also made by G. Preuner, and J. Brockmöller. R. F. Bacon noted that the combination is favoured by pressure. F. Pollitzer gave for the reaction $H_2+S_{solid}=H_2S$, $[H_2]=K[H_2S]$, where the bracketed symbols refer to partial press.; he found that log $K=-5000/4{\cdot}571T-1{\cdot}4$. S. Dushman studied this reaction. D. Alexejeff gave for the percentage degree of dissociation, $x=5{\cdot}5$ at 1023° K.; 8·7 at 1103° K.; 15·6 at 1218° K.; 24·7 at 1338° K.; and 30·7 at 1405° K.; and $\frac{1}{2}x^3(1-x)^{-2}=K_p$. A. Geitz studied the reaction in the high-tension arc flame. According to J. Milbauer, the rate of formation of hydrogen sulphide from hydrogen and molten sulphur is not affected by the presence of a sulphide of silver, gold, mercury, thallium, arsenic, molybdenum, or by metallic mercury or palladium, but was increased by platinum black, or red phosphorus. The acceleration in the latter case is possibly due to the occurrence of the following reactions: $P_2S_5+8H_2=2PH_3+5H_2S$, and $2PH_3+4S_2=P_2S_5+3H_2S$. The rate of formation of hydrogen sulphide by the action of hydrogen on sulphur alone increases continuously with rise of temp., but in presence of red phosphorus the maximum rate is attained at 218°, after which it diminishes up to 278°. The rate of formation in the case of sulphur and hydrogen alone is greater when the sulphur has been heated almost to boiling and then cooled to 278°, which indicates that the transformation $S_8\rightleftharpoons 4S_2$ takes place more slowly than $S_2\rightleftharpoons 2S$. T. J. Drakeley observed that hydrogen sulphide is formed when hydrogen is passed over heated pyrites. H. Buff and A. W. Hofmann observed that an electrically heated spiral of platinum or iron wire decomposes hydrogen sulphide, forming in the latter case ferrous sulphide. On the one hand, G. Chevrier observed that sulphur vapour and hydrogen unite under the stimulus of electric sparks; A. Boillot obtained hydrogen sulphide by passing sparks between platinum wires covered with sulphur in hydrogen; while W. R. Grove made analogous observations. On the other hand, H. Davy, B. Lepsius, and H. Buff and A. W. Hofmann observed that hydrogen sulphide is decomposed by the passage of electric sparks through the gas. M. Berthelot also represented the reaction with the silent discharge: $8H_2S=7H_2+H_2S_n+(8-n)S$. R. Schwarz and P. W. Schenk observed an activation of sulphur vapour under the influence of the silent discharge; and R. Schwarz and W. Kunzer observed that with the silent discharge (8000 volts), the percentage proportion of hydrogen sulphide decomposed was

	20°	270°	390°	430°
Decomposition . .	27·17	2·30	1·14	2·30 per cent.

showing that the amount decomposed decreases with rise of temp., but as the temp. approaches the b.p. of sulphur, there is a back reaction. The re-formation of hydrogen sulphide is attributed to the activation of sulphur vapour by the discharge. C. Montemartini observed the synthesis of hydrogen sulphide from its elements in the corona discharge.

Hydrogen sulphide is produced when nascent hydrogen acts on sulphur. Thus, E. Becquerel obtained it at the cathode during the electrolysis of water with the electrodes in contact with sulphur—sulphuric acid was formed at the anode. P. Fischer obtained the gas by the electrolysis of soln. of sulphides. A. Cossa also obtained it by the electrolysis of water with finely-divided sulphur in suspension; S. Cloez, by the action of hydrochloric acid on zinc, aluminium, or iron when sulphur is suspended in the acid—the best yield was obtained with aluminium; the worst, with zinc; and E. Trautman used in a similar manner tin or stannous chloride and hydrochloric acid, or zinc and acetic acid as the source of hydrogen, and he found the yield was greater in the presence of a solvent for sulphur—*e.g.* acetic acid or alcohol. The yield with acetic acid was better than with alcohol. A. Bach found that recently-melted platinum contains adsorbed sulphur compounds and evolves hydrogen sulphide when heated in hydrogen; according to experimental conditions, this power is more or less rapidly lost. Passage of the evolved hydrogen over powdered sulphur does not increase the amount of hydrogen sulphide produced from the fresh metal, and does not cause formation of hydrogen sulphide after the metal has become "aged." Treatment of the "aged" metal with ordinary laboratory air restores its ability to give hydrogen sulphide when heated in hydrogen; under similar conditions, no trace of hydrogen sulphide is produced after treatment with carefully purified air. The phenomenon of "resting" depends, therefore, on the adsorption of sulphur compounds from the air. Palladium-sponge behaves similarly to platinum.

Sulphur vapour has an absorption band in the ultra-violet at 1750 A., and R. G. W. Norrish found that ultra-violet radiation of wave-lengths of about 2700 A. is photochemically active in initiating a gaseous reaction between hydrogen and sulphur vapour, proportional to the press. of the sulphur vapour. In the gaseous state, reactions between hydrogen and sulphur can take place only between sulphur atoms, which are produced both by collisions and by photochemical dissociation. In addition, a reaction at the surface takes place between hydrogen and activated S_8-molecules, and is not affected by ultra-violet radiation, the activation being entirely caused by collisions. In all cases, whether the activation takes place in the gaseous state or at the surface, by radiation or by collision, the energy of activation is constant, indicating that, in activation by collisions, the Newtonian laws of inelastic impact do not apply, but that the process obeys the laws of quantum dynamics, the same amount of energy being extracted from the colliding molecules, whatever the force of their impact, providing this exceeds a certain magnitude. In these reactions, activation of the sulphur molecule, whether S_2 or S_8, is synonymous with the disruption of one valency "bond."

The formation of hydrogen sulphide by the action of water or steam on sulphur has already been discussed in connection with elemental sulphur. C. A. Burghardt obtained hydrogen sulphide by heating water with iron pyrites in a sealed tube. P. Hautefeuille obtained hydrogen sulphide by the action of sulphur on gaseous or a conc. aq. soln. of hydrogen iodide. The reaction is reversible in the cold, for the hydrogen sulphide also reacts with the soln. of iodine in hydriodic acid, forming sulphur. F. Pollitzer found for the equilibrium constant K of the reaction $H_2S+2I_{solid} \rightleftharpoons 2HI+S_{solid}[HI]^2=K[H_2S]$, where the bracketed symbols refer to partial press.; $K \times 10^3=1{\cdot}90$ at 40·1°; 4·50 at 20·1°; 9·96 at 60·2°; and 47·0 at 80·7°. The heat of the reaction is 17·2 Cals. F. Pollitzer also examined the equilibrium conditions of the reaction in aq. soln.

M. J. Fordos and A. Gélis [8] obtained hydrogen sulphide by boiling sulphur with an aq. soln. of an alkali sulphide; and A. Girard, by boiling a soln. of sodium sulphide, or a soln. of sodium pyrophosphate and sulphur. D. Urquhart obtained hydrogen sulphide by the action of superheated steam on barium or strontium sulphide. J. Böhm said that the lower sulphides of the alkalies and alkaline earths give hydrogen sulphide when boiled with water; while pyrites, galena, and zincblende require a temp. of 150°–200°. F. Meissner observed that this gas is formed in roasting metal sulphides in the presence of superheated steam. Water decomposes sulphide of phosphorus or boron (*q.v.*) with the evolution of hydrogen sulphide. P. de Clermont and J. Frommel observed that some hydrogen sulphide is formed when arsenic trisulphide is boiled with water, but with arsenic disulphide, only a little hydrogen sulphide appears at the beginning—*vide* arsenic trisulphide; and for the preparation of hydrogen sulphide by the action of conc. hydrochloric acid on antimony trisulphide, *vide* antimony trisulphide. Under ordinary laboratory conditions, hydrogen sulphide is prepared by the action of acids on the metal sulphides. C. W. Scheele recommended ferrous sulphide and sulphuric acid, and this method is in common use to-day. Hundreds of different forms of apparatus—typified by the familiar Kipp—have been devised in which the acid acts on the sulphide contained in a vessel, so arranged that when the exit tube of the apparatus is closed by a stopcock, the pressure of the gas drives the acid from the sulphide, and gas is no longer generated. When the stopcock is opened, the pressure of the gas is released, and the acid returns to the sulphide to generate more gas as required —*e.g.* Fig. 9, **2**. 18, 6. The apparatus can also be arranged so that the acid is added as required, *viâ* a tap, from the top of a tower containing the sulphide the exhausted acid drains away at the bottom. The same source of hydrogen sulphide was recommended by C. D. Tourte, J. L. Gay Lussac, and numerous others. S. Kitashima said that if free sulphur is present it is converted into hydrogen sulphide if a large quantity of iron is present in the sulphide. G. Dragendorff recommended artificial ferrous sulphide prepared with purified materials in order to obtain hydrogen sulphide of a high degree of purity. E. W. Parnell and J. Simpson treated ammonium sulphide with carbon dioxide or ammonium hydrocarbonate; and H. N. Draper passed the ammonium sulphide vapours—a by-product in the ammonia-soda process—into dil. sulphuric acid. R. Finkener, and W. Hampe used arsenic-free sulphuric acid and sodium sulphide; C. F. Mohr treated barium sulphide and hydrochloric acid—F. W. Martino recommended a barium sulphocarbide made by fusing barium sulphate and carbon in the electric furnace. R. Otto, and J. Habermann recommended using calcium sulphide and hydrochloric acid. C. R. Fresenius employed a mixture of calcium sulphide and sulphate moulded into cubes for use in Kipp's apparatus. G. Bong, B. Kosmann, and F. R. L. Wilson treated the alkaline earth sulphide with carbon dioxide. H. von Miller and C. Opl, and J. R. Michler treated a soln. of calcium hydrosulphide with steam; E. Divers and T. Shimidzu, F. Gerhard, and G. Sisson, heated a soln. of magnesium hydrosulphide; and J. Habermann gently warmed a mixture of magnesium chloride and calcium sulphide mixed with a little water: $MgCl_2+CaS+2H_2O=Mg(OH)_2+CaCl_2+H_2S$. H. Hager, and H. Howard treated zinc sulphide with hydrochloric acid. H. Howard devised a process for producing hydrogen sulphide from complex zinc sulphide ores and sulphuric acid. P. Casamajor, W. P. Jorissen, and W. Skey found that hydrogen sulphide is formed when a mixture of galena (lead sulphide), iron pyrites, or bismuth sulphide is treated with zinc and dil. hydrochloric acid, but these sulphides are not attacked in the absence of the zinc; and F. Stolba, by treating the lead sulphide with a soln. of hydrochloric acid and sodium chloride. H. Fonzes-Diacon recommended using water and aluminium sulphide as a source of the gas. H. Wiederhold obtained hydrogen sulphide by decomposing sulphides or hydrosulphides by humic acid or substances containing humic acid—*e.g.* peat.

Hydrogen sulphide was obtained from the sulphide in the manufacture of soda-ash. H. Grouven, for instance, passed steam over the sulphide residue at a high temp. This subject was investigated by L. Mond, G. Lunge, M. Schaffner and W. Helbig, C. Stahlschmidt, G. Guckelberger, T. Rowan, J. Mactear, F. B. Rawes, J. W. Kynaston, W. Weldon, C. Opl, E. W. Parnell and J. Simpson, C. Kraushaar, G. Aarland, A. R. Pechiney, etc.

Hydrogen sulphide is also formed by reducing the oxy-acids with sulphur—*e.g.* by the action of hydrogen on some metals on dil. sulphurous or sulphuric acid. Thus, S. Rosenblum obtained it by the action of iron on a soln. of calcium sulphate in carbonic acid; and A. Hartmann, by passing a mixture of steam and sulphur dioxide through red-hot coke. H. Highton reported that hydrogen sulphide was formed as from the carbon in a cell charged with dil. sulphuric acid and having zinc for the positive plate and carbon packed in granulated carbon for the negative. There is a possibility that the hydrogen sulphide was due to the contamination of the carbon with iron sulphide, or, according to W. Skey, of adsorbed hydrogen sulphide.

A number of carbon compounds furnish hydrogen sulphide when treated with water or steam—*e.g.* carbon disulphide, **6**. 39, 42; thiocyanic acid or potassium thiocyanate, as observed by F. Sestini and A. Funaro, and J. T. Conroy and co-workers; mercaptan and alcohol with sodium sulphide, as observed by R. Böttger; boiling ethyl malonate and sulphur, as found by A. Michael; and boiling milk, as reported by L. Schreiner, and F. Utz. C. W. Scheele prepared hydrogen sulphide by heating a mixture of olive oil and sulphur; H. Reinsch, sulphur and suet; J. Galletley, W. C. Ebaugh, A. Henwood and co-workers, J. Fletcher, W. Johnstone, A. P. Lidoff, and H. Wuyts and A. Stewart, sulphur and paraffin—A. Henwood gave 36 parts sulphur, 14 parts of paraffin oil boiling above 110°, and 50 parts asbestos fibre; E. Bindschedler and E. W. Rugeley, hydrocarbon oil and sulphur; P. Champion and H. Pellat, A. Étard and H. Moissan, and P. Mochalle, sulphur and sugar; A. C. Vournasos, by heating a mixture of sulphur and sodium formate to 400°, likewise also a mixture of sodium sulphite and formate; and E. Prothière, sulphur and vaseline. T. J. Drakeley observed the formation of hydrogen sulphide by passing sulphur dioxide over heated coal; by heating mixtures of coal and sulphur; and by heating mixtures of coal and iron pyrites. F. W. Sperr[9] extracted hydrogen sulphide from the gas resulting from the cracking of petroleum.

Hydrogen sulphide is formed during the putrefaction of organic matter containing sulphur by the agency of bacteria. Hence, its occurrence in the gases of the alimentary tract—*vide supra.* The bacteria concerned in the reduction of albuminates, etc., to hydrogen sulphide were described by P. Miquel, J. Thomann, T. Sasaki and I. Otsuka, M. Hausmann, P. N. Holschewnikoff, M. Debraye and M. Legrain, etc. The formation of sulphur or of hydrogen sulphide by the reduction of sulphates with organic matter has been known for a long time. Thus, K. W. G. Kastner showed that if a soln. of calcium or sodium sulphate be mixed with a little sugar, gum, glycerrhizin, and allowed to stand in a closed vessel for a couple of years, there is formed hydrogen sulphide, carbon dioxide, and acetic acid; straw also develops hydrogen sulphide when in contact with mineral waters if air has access, but not if air be excluded. A. Vogel noted a similar phenomenon with beechwood. Many mineral waters were found by K. W. G. Kastner, G. Bischof, and J. W. Döbereiner to contain sufficient organic matter to decompose the sulphates in soln. O. Henry observed a similar result with the sulphate water from Passy, and from the neighbourhood of Paris. At the same time, ferrous sulphide, and slimy flakes of an azotized organic substance were produced. The hydrogen sulphide in sulphur springs is derived from the decomposition of alkaline sulphates by organic matter; moist clay containing gypsum and organic matter likewise furnishes hydrogen sulphide. According to J. F. Daniell, the waters of the rivers in hot climates, say the west coast of Africa, may be highly charged with organic matter, this mixing with sea-water containing sulphates, may give rise to hydrogen sulphide—sometimes at a distance of 27 miles from the mouth of the rivers. The water has been reported to contain 6 cubic inches of gas per gallon. G. J. Mulder attributed the reduction of sulphates to the hydrocarbons formed by the decomposing organic matter; R. J. Petri and A. Maassen, to hydrogen in *statu nascendi*; and E. Plauchud, to the growth of algæ. A. Étard and L. Olivier, and F. Cohn attributed the action to algæ or bacteria. This subject was discussed by A. van Delden, A. Fitz, N. Gosling, F. Hoppe-Seyler, J. F. Liverseege, R. H. Saltet, S. Winogradsky, etc. The *spirillum desulfuricans* of W. M. Beijerinck reduces sulphates to hydrogen sulphide—*vide supra,* sulphur bacteria. E. Pollacci, L. Olivier, and J. Böhm observed that this gas is formed when sulphur is in the vicinity of certain growing plants; and M. E. Pozzi-Escot observed that it is produced by the action of the hydroxygenases—*e.g.* philothion—on sulphur. The formation of hydrogen sulphide during alcoholic fermentation by yeast has been discussed by J. de Rey-Pailhade, E. Crouzel, M. E. Pozzi-Escot, R. Schander, H. Will and co-workers, H. Wanderscheck, L. Sostegni and A. Sannino, J. E. Abelous and H. Ribaut.

The hydrogen sulphide derived from ferrous sulphide and dil. sulphuric acid contains phosphine, arsine, etc.[10] When the gas is required of a high degree of purity, it is best made from purified materials—say by heating to about 60° a mixture of calcium sulphide with a sat. soln. of magnesium chloride, and drying the gas over phosphorus pentoxide. The rate of the reaction is regulated by raising or lowering the temp. of the flask. W. Lenz[11] recommended removing arsine by washing the gas with hydrochloric acid in a train of four wash-bottles—but H. Hager, and R. Otto did not consider the purification satisfactory. O. von der Pfordten removed arsine by passing the gas over potassium trisulphide at 300°–350° : $2AsH_3+3K_2S_3=2K_3AsS_3+3H_2S$; and O. G. Jacobsen, and Z. H. Skraup passed the gas over solid iodine which fixed the arsine as arsenic triiodide, and the iodine vapour was removed by washing the gas with water. O. van der Pfordten removed oxygen by washing it with chromous chloride. A. Gautier purified the gas from arsine by washing the gas with water, passing it through a short tower containing moistened pumice-stone, then along a tube containing small fragments of glass maintained at a low red-heat, then through a serpentine wash-bottle containing barium sulphide soln., and finally through cotton-wool. H. Moissan first solidified the gas, then exhausted the containing vessel by means of a mercury pump, and then allowed the gas to regain the ordinary temp.—**2.** 18, 8. E. Cardoso discussed the purification of the gas.

The physical properties of hydrogen sulphide.—This compound at ordinary temp. is a colourless gas with the offensive odour characteristic of rotten eggs. It has been condensed to a liquid, and frozen to a solid. The **vapour density** of the gas, air unity, when calculated from the equation: H_2(2 vols.)+S_{gas}(1 vol.) $=H_2S$(2 vols.), is 1·1769. T. Thomson[12] observed 1·1791 ; J. L. Gay Lussac and L. J. Thénard, 1·1912 ; L. J. Thénard, 1·236 ; H. Davy, 1·267 ; L. Bleekrode, 1·191 at 18·5° ; and A. Leduc, 1·1895±0·0004. G. Baume and F. L. Perrot found that a litre of gas, at 0° and 760 mm., weighs 1·5392 grms. ; and F. Exner calculated 1·5223 grms. The literature was reviewed by M. S. Blanchard and S. F. Pickering. M. Faraday gave 0·9 for the **specific gravity** of the liquid ; L. Bleekrode, 0·91 at 18·5° ; R. de Forcrand and H. Fonzes-Diacon, 0·86 at the b.p. ; and D. McIntosh and B. D. Steele, 0·964 at the b.p. The results of B. D. Steele and co-workers are indicated below ; so that the sp. gr. D at T° K. are represented by the formula $D=0{\cdot}964\{1+0{\cdot}00169(60{\cdot}3-T)\}$. The **molecular volume** at the b.p., given by B. D. Steele and co-workers, is 35·2. G. M. Maverick found for the **compressibility** of hydrogen sulphide for $p=746{\cdot}872$, 370·877, and 248·987, respectively $v=166{\cdot}646$, 337·310, and 502·269, and $pv=124463{\cdot}5$, 125100·6, and 125307·6. Hence, $1+\lambda=(pv)_0/(pv)_{760}=124440{\cdot}9/125730{\cdot}4=1{\cdot}01036$. P. A. Guye and L. Friedrich gave for the **constants of J. D. van der Waals' equation**—**1.** 13, 4—$a=0{\cdot}00887$ and $b=0{\cdot}00191$ when referred to the initial vol. of the gas ; $a=4{\cdot}4\times10^6$, and $b=42{\cdot}5$ when referred to gram-molecules ; and $a=3780$, and $b=0{\cdot}870$ when referred to grams. M. Faraday said that the solid has a greater sp. gr. than the liquid. R. de Forcrand and H. Fonzes-Diacon calculated 39·53 for the **molecular volume** in the liquid state. This subject was also examined by E. Rabinowitsch, who gave 35·4 for the constant ; and also by R. Lorenz and W. Herz. Analyses by J. J. Berzelius, J. L. Gay Lussac and L. J. Thénard, and L. J. Thénard agree with the formula H_2S, and this is in harmony with the vap. density. F. Exner calculated for the **molecular diameter,** 22×10^{-9} cm. ; and 60×10^{-7} cm. for the **mean free path ;** and T. Graham, $37{\cdot}5\times10^{-7}$ cm. T. Graham gave 469×10^2 sq. cms. for the total sectional area of all the molecules in a c.c. of gas, at 0° and 760 mm. ; and 41,190 cms. per second for the **molecular velocity.** A. O. Rankine and C. J. Smith calculated $0{\cdot}773\times10^{-15}$ cm. for the collision area. T. Graham's experiments, calculated by O. E. Meyer and A. von Obermayer, gave for the **viscosity** of the gas, at 0°, $\eta=0{\cdot}0001154$ at 0° and 0·0001300 at 20° ; O. E. Meyer, 0·000137 when air is 0·000200 ; O. E. Meyer and F. Springmühl gave 0·000130 (air 0·000212) between 10° and 20° ; and A. O. Rankine and C. J. Smith, 0·0001175 at 0°, and 0·0001610 at 100°. D. McIntosh and B. D. Steele gave for the viscosity, η, of the liquid :

	−82°	−79·7°	−74·8°	−71·8°	−66·9°	−63·2°
η . .	0·547	0·528	0·510	0·488	0·470	0·454

and for the temp. coeff. of the viscosity, 1·10. J. E. Lewis measured the viscosity of hydrogen sulphide in chloroform. B. D. Steele and co-workers obtained the following results for the sp. gr. of the liquid, D; the vapour density, D_v; the **surface tension,** σ dynes per cm.; and the mol. **surface energy,** $\sigma(Mv)^{\frac{2}{3}}$ ergs:

	−84°	−78·4°	−73·3°	−69·1°	−62·2°
D . .	1·006	0·997	0·987	0·9806	0·9692
D_0 . .	0·00055	0·00076	0·00098	0·00122	0·00175
σ . . .	33·418	32·126	31·020	30·448	28·783
$\sigma(Mv)^{\frac{2}{3}}$ . .	349·5	338·0	328·3	324·7	308·6

There was no evidence of molecular association observed during these determinations. B. Tamamushi studied the effect of hydrogen sulphide on the surface tension of water. F. Schuster calculated 2545 atm. for the **internal pressure** of the liquid. A. Masson gave for the **velocity of sound** in the gas 289·3 metres per sec. at 0°. N. de Kolossowsky studied the relation between the velocity of sound and the translation velocity of the molecules. F. J. von Wisniewsky, and H. Remy discussed the structure of hydrogen sulphide; H. Henstock, and F. Hand, the **electronic structure;** and A. O. Rankine, and F. J. von Wisniewsky, the general structure of the molecules of the family of hydrides. A. Hagenbach calculated the coeff. of **diffusion** of hydrogen sulphide in aq. soln. to be 1·24 sq. cms. per day at 15·5°, and F. Exner gave 1·53 at 16°. The subject was studied by G. Tammann and V. Jessen. A. Eucken gave 0·03045 cal. per cm. per second per degree for the **thermal conductivity** of hydrogen sulphide at 0°.

M. Croullebois[13] gave for the **specific heat** of the gas, at constant press., 0·2423; and for the ratio of the two sp. hts., C_p/C_v, P. A. Müller gave 1·2759 between 10·2° and 40·0°, and between 259 mm. and 767·4 mm.; J. W. Capstick gave 1·340, or $C_p=8\cdot237$, and $C_v=6\cdot170$; R. Thibaut, at 20°, 1·32 at $\frac{1}{3}$ atm. press., and 1·34 at one atm. press. corresponding respectively with $C_p=8\cdot179$ and 8·100, and $C_v=6\cdot166$ and 6·036. A. Masson's results furnish 1·313 for the ratio of the two sp. hts., and $C_p=8\cdot728$, and $C_v=6\cdot45$; H. V. Regnault, $\gamma=1\cdot326$, $C_p=8\cdot290$, and $C_v=6\cdot253$; R. W. Millar's results agree with $\gamma=1\cdot308$, $C_p=8\cdot831$, and $C_v=6\cdot750$. G. N. Lewis and M. Randall gave $C_p=8\cdot81-0\cdot0019\theta+0\cdot0_5222\theta^2$.

M. Faraday[14] liquefied the gas by enclosing sulphide of iron and conc. hydrochloric acid in one leg of a sealed V-tube, when the other leg is cooled by a freezing mixture. J. H. Niemann said that the ferrous sulphide must have no free iron or else the hydrogen liberated will burst the tube. Instead of ferrous sulphide and acid, G. Kemp, J. von Liebig, and R. Bunsen used hydrogen persulphide; and H. J. F. Melsens, charcoal sat. with the gas. M. Faraday also obtained the liquid by passing the gas through a tube cooled by a mixture of solid carbon dioxide and ether; and when this freezing mixture is evaporated in vacuo, the clear, colourless, mobile liquid freezes to a snow-white mass of crystals. M. Faraday found that the gas liquefied at the following temp. and press.:

	−70°	−40°	−3·33°	11·11°	0°	18°	50°	100°
Press. .	1·09	2·86	6·36	14·60	10·25	16·95	35·56	88·7 atm.

The four last data are by C. Olschewsky. O. Maass and D. McIntosh gave for the **vapour pressure,** p:

	−110·0°	−99·7°	−90·6°	−87·7°	−80·9°	−72·0	−64·7°	−60·1°	−58·1°
p .	18	43	91	112	188	393	573	732	822 mm.

H. V. Regnault represented the vap. press. by $\log p=4\cdot2038661-0\cdot7960525\alpha^{\theta+27}$, where $\log \alpha=\bar{1}\cdot9895941$; C. Antoine, by $\log p=0\cdot72176\{9\cdot6282-1000/(\theta+238)\}$. E. Cardoso represented his results:

	0°	10°	20°	40°	60°	80°	100°	100·4°
p .	10·20	13·34	17·24	27·80	42·22	61·38	88·32	88·92 atm.

by formulæ of the type $p=ae^{b\theta+c\theta^2}$ atm.; for temp. between 0° and 50°, he gave $\log p=1\cdot00860+0\cdot011935\theta-0\cdot0002683\theta^2$, and between 50° and 100·4°, $\log p$

$=1·53820+0·0088786(\theta-50)-0·000014429(\theta-50)^2$. The two parabolas join perfectly at 50°. From these formulæ, $dp/d\theta=p(0·027481-0·000123710)$, and $dp/d\theta=p\{0·020444-0·000066449(\theta-50)\}$. B. D. Steele and L. S. Bagster studied the vap. press. of the binary systems: H_2S–HBr, and H_2S–HI. U. Antony and G. Magri said that the liquid vaporizes slowly without boiling. M. Faraday gave −73° for the **boiling point** at 760 mm.; H. V. Regnault, −61·8° at 755 mm.; C. Olschewsky, −63·5°; A. Ladenburg and C. Krügel, −60·4° at 755·2 mm.; R. de Forcrand and H. Fonzes-Diacon, −61·6° at 760 mm.; D. McIntosh and B. D. Steele, −60·1°; O. Maass and D. McIntosh, −59·8°; R. de Forcrand and H. Fonzes-Diacon, −61° at 773 mm.; and E. Cardoso and E. Arni, −60·2° at 760 mm. N. de Kolossowsky gave 0·63 to 0·72 for the **ebulliscopic constant** of the liquid. M. Faraday gave −85° for the f.p.; E. Cardoso and E. Arni, −83°; and O. Maass and D. McIntosh, −83·6°, and B. D. Steele and co-workers, −82·9° for the **melting point.** R. de Forcrand and H. Fonzes-Diacon gave −86° for the m.p. E. Cardoso gave 100·4° for the **critical temperature;** and A. A. Schnerr, 100·43°, while J. Dewar, and P. A. Guye gave 100·2° for the critical temp., and 92·0 atm. for the **critical pressure;** C. Olschewsky gave respectively 100° and 88·7 atm.; A. Leduc and P. Sacerdote, 100° and 90 atm.; F. E. C. Scheffer, 99·6° and 88·3 atm. and E. Cardoso and E. Arni, 100·40° and 89·05 atm. D. A. Goldhammer gave 0·00490, and F. Schuster, 0·00413 for the **critical volume.** S. F. Pickering gave for the best representative values $T_c=373·5°$ K.; and $p_c=89$ atm. R. de Forcrand and H. Fonzes-Diacon found the latent **heat of vaporization** to be 4230 cals., and 20·01 for **Trouton's number.** O. Maass and D. McIntosh gave $19·3\times10^{10}$ ergs or 4585·8 Cals. per mol., or 134·6 Cals. per gram for the latent heat of vaporization, while P. H. Elliot and D. McIntosh gave $19·6\times10^{10}$ ergs; and A. A. Schnerr, 449·8 Cals. per mol., or 131·98 Cals. per gram at −61·37°. F. Paneth and E. Rabinovitsch discussed some relations between the physical properties of the family of hydrides.

J. Thomsen [15] gave for the **heat of formation** $(H_2,S_{solid})=H_2S_{gas}+4·510$ Cals.; P. Hautefeuille, 4·82 Cals.; and M. Berthelot, for $(H_2,S_{gas})=7·2$ Cals. The subject was studied by R. de Forcrand. J. Thomsen gave 136·71 Cals. for the **heat of combustion** at constant press. R. de Forcrand and H. Fonzes-Diacon gave 16·34 Cals. for the heat of formation of the solid hydrate. J. Thomsen gave 4·76 Cals. per mol. for the heat of absorption; and 4·75 Cals. for the **heat of solution** of a mol. in 900 vols. of water. For the heat of formation of the hydrate, *vide infra.* J. Thomsen, P. A. Favre and J. T. Silbermann, and M. Berthelot measured the thermal value of the reaction between hydrogen sulphide and the metal oxides; J. Thomsen, and P. Sabatier, the heat of formation of the metal sulphides; and J. Thomsen, the heat of the decomposition of the metal nitrates by hydrogen sulphide. K. Jellinek and A. Deubel calculated the **chemical constant,** −0·79, of hydrogen sulphide.

J. B. Biot and D. F. J. Arago [16] gave 1·000636 for the **index of refraction** of the gas, and P. L. Dulong gave 1·000641 for white light; L. Bleekrode, and M. Croullebois gave 1·000639 for Na-light, and E. Mascart, 1·000619. C. and M. Cuthbertson gave 1·0006509 for light of wave-length $\lambda=846·1\mu\mu$; 1·0006440 for $\lambda=546·1\mu\mu$; 1·0006412 for $\lambda=579·0\mu\mu$; and 1·0006362 for $\lambda=656·3\mu\mu$. C. and M. Cuthbertson found that the refractivity of hydrogen sulphide is about 6 per cent. less than is required by the addition law. The number of dispersion electrons in hydrogen sulphide is not equal to the sum of those in the component atoms. M. Faraday, and J. H. Niemann observed that the refractory power of liquid hydrogen sulphide is greater than that of water. J. Dechant gave 1·374 for the refractive index of the liquid for Na-light; and L. Bleekrode, 1·380 at 12·5°, and 1·384 at 18·5° for Na-light, and 1·390 at 18·5° for sunlight. The sp. refraction with the μ-formula is 0·429, and with the μ^2-formula, 0·262. The subject was studied by T. H. Havelock. C. V. Raman and N. S. Krishnan gave $0·26\times10^{-10}$ for **Kerr's constant** at one atm. press., 20°, and the *D*-line. K. R. Ramanathan and N. G. Srinivasan investigated the optical anisotropy of hydrogen sulphide. A. Kundt and W. C. Röntgen studied the **electromagnetic rotation** of the plane of polarized light. K. R. Ramanthan and N. G. Srinivasan found that the depolarization of light in a direction perpendicular to the incident beam in hydrogen sulphide is the same as in hydrogen chloride and ammonia (*q.v.*). J. Piccard and E. Thomas discussed the colour of sulphide ions. W. H. Bair,[17] and H. Deslandres studied the **spectrum** of hydrogen sulphide. G. D. Liveing and J. Dewar, W. A. Miller, P. Baccei, L. Ciechomsky, and W. H. Bair investigated the **ultra-violet spectrum**; and A. H. Rollefson, S. C. Garrett, J. Tyndall, and W. W. Coblentz the **ultra-red spectrum.** The maxima in the absorption bands occur at $4{\cdot}24\mu$, $5{\cdot}6\mu$, $7{\cdot}12\mu$, $7{\cdot}78\mu$, $8{\cdot}46\mu$, $9{\cdot}65\mu$, $10{\cdot}08\mu$, $10{\cdot}6\mu$, and $10{\cdot}95\mu$. J. W. Ellis discussed the spectra of compounds with S–H linkages. R. Wright found that while the strong acids give the same absorption spectrum as their sodium salts, the reverse is the case with weak acids like aq. soln. of hydrogen sulphides. It is supposed that the non-ionized molecule—capable of ionization—is in a state of stress and is more absorptive than a similar free ion, or than a molecule incapable of ionization.

A. S. Eve found that the ionization produced in the gas by **X-rays** is 0·9 (air unity), and by the **γ-rays** of radium, 1·23. According to E. Wourtzel, when hydrogen sulphide is exposed to **radium rays,** the ratio of the amount of hydrogen formed to the amount of radiation destroyed diminishes with the time of exposure owing to diminution in press. caused by decomposition of the hydrogen sulphide. The calculated amount of hydrogen formed, corresponding with the total destruction of the emanation and the complete use of its radiation, is constant. The velocity of decomposition diminishes with the temp. The number of molecules of hydrogen sulphide decomposed by the radiation from the emanation exceeds 3·3 times the number of ions produced in air under the same conditions. The relative amounts of water and hydrogen sulphide decomposed by a given amount of radiation are as 1 : 4·7, expressed as mols. E. Wourtzel also studied the decomposition of the gas, $H_2S=H_2+S$, by exposure to the α-rays of radium. R. A. Morton and R. W. Riding gave 11·3 for the **ionizing potential**; and C. A. Mackay, 10·4 volts. L. B. Loeb and L. du Sault studied the mobilities of the gaseous ions; and J. H. Bartlett, ionization by slow electronic impacts.

The effect of the **electrical discharge** on the gas has already been discussed. J. J. Thomson[18] found the **electrical conductivity** of the gas to be very small. A. de Hemptinne said that the flame of burning hydrogen sulphide is a good electrical conductor. U. Antony and G. Magri, and L. Bleekrode made a similar remark about the conductivity of the dry liquid. B. D. Steele and co-workers gave $0{\cdot}1\times10^{-6}$ ohm for the sp. conductivity of the liquid when that of the purest water is $0{\cdot}04\times10^{-6}$ ohm. The aq. soln. of hydrogen sulphide is very little ionized: $H_2S\rightleftharpoons H^{\cdot}+HS'$, and this is reduced in the presence of the stronger acids. This, said W. Ostwald, is connected with the solvent action of acids on certain sulphides, and the low solubility of the metal sulphides in water. The sulphides of the univalent metals are also ionized: $R_2S=2R^{\cdot}+S''$; and also $R_2S+H_2O=2R^{\cdot}+SH'+OH'$.

TABLE II.—RELATIVE CONCENTRATIONS OF THE IONS IN AQUEOUS SOLUTION OF THE SULPHIDES.

Soln.	S''	HS'	H_2S	$H^{\cdot}$	OH'
Mol	0·09	0·91	$1{\cdot}3\times10^{-7}$	$1{\cdot}3\times10^{-14}$	0·91
Mol NaHS	36×10^{-5}	1·0	$3{\cdot}6\times10^{-4}$	$3{\cdot}3\times10^{-11}$	$3{\cdot}6\times10^{-4}$
Mol $(NH_4)_2S$	3×10^{-6}	1·0	5×10^{-2}	$0{\cdot}5\times10^{-2}$	$1{\cdot}7\times10^{-5}$
Mol $NH_4(HS)$	$1{\cdot}6\times10^{-7}$	0·93	0·07	$0{\cdot}7\times10^{-8}$	$1{\cdot}7\times10^{-6}$
Sat. H_2S in water	$1{\cdot}2\times10^{-15}$	$0{\cdot}95\times10^{-4}$	0·1	$0{\cdot}95\times10^{-4}$	$1{\cdot}3\times10^{-10}$
Sat. H_2S in *N*-CH_3COOH	$0{\cdot}6\times10^{-18}$	$2{\cdot}0\times10^{-6}$	0·1	4×10^{-3}	3×10^{-14}
Sat. H_2S in *N*-HCl	$1{\cdot}1\times10^{-23}$	$0{\cdot}91\times10^{-8}$	0·1	1	$1{\cdot}2\times10^{-14}$

According to J. Knox, the proportion of H_2S, and of S''-, HS'-, $H^{\cdot}$-, and HO'-ions in aq. soln. of the sulphides is indicated in Table II. K. Jellinek and J. Czerwinsky measured the conc. of the ions in the hydrolysis equilibrium of sodium sulphide, and found that

	NaS	NaS'	Na'	$S^{\cdot}$	OH'	SH'	$H^{\cdot}$	NaOH	NaSH
0·1*N*- .	0·0003	0·002	0·08	0·006	0·035	0·033	30×10^{-15}	0·004	0·0055
1·06*N*- .	0·053	0·09	0·66	0·076	0·226	0·195	48×10^{-15}	0·084	0·115
2·85N- .	0·431	0·47	1·26	0·259	0·131	0·138	8×10^{-15}	0·133	0·126

With 0·1*N*-NaHS, NaSH, 0·085 ; S'', $3{\cdot}2\times10^{-6}$; $H^{\cdot}$, $6{\cdot}3\times10^{-11}$ and OH', $8{\cdot}0\times10^{-5}$. The degree of hydrolysis of sodium sulphide is :

N . .	0·1	0·21	0·53	1·06	1·59	2·12	2·85
Hydrolysis	0·805	0·754	0·655	0·585	0·535	0·500	0·460

The percentage hydrolysis of 0·1*N*-NaSH is 0·15 per cent. at 0°, 0·08 per cent. at 10°. The temp. coeff. and the heats of hydrolysis are small; and the heat of ionization of HS' is large—about 13,000 cals. For the **ionization constant** of aq. soln. of hydrogen sulphide : $H_2S \rightleftharpoons H^{\cdot}HS'$, at 18°, M. de Hlasko, and F. Auerbach gave $0{\cdot}91\times10^{-7}$, which is between the value $0{\cdot}574\times10^{-7}$, at 18°, given by J. Walker and W. Cormack, and the $1{\cdot}2\times10^{-7}$ given by T. Paul. K. Jellinek and J. Czerwinsky gave 1×10^{-7}, at 0°. J. Knox calculated the second ionization constant to be $1{\cdot}2\times10^{-15}$ at 25°; M. Aumeras, $0{\cdot}37\times10^{-15}$ to $0{\cdot}59\times10^{-15}$ at 25°; and K. Jellinek and J. Czerwinsky gave 2×10^{-15} at 0°; and for the ionic mobility they gave 42·5 at 0°, 56·5 at 18°, and 64 at 25° for HS'-ions at infinite dilution. M. Randall and C. F. Bailey studied the activity coefficient of hydrogen sulphide. R. E. Hughes found that thoroughly dried hydrogen sulphide gas has no action on litmus; but the gas reddens tincture of litmus, although the red colour disappears on exposure to air. F. J. Malaguti said that tincture of litmus, saturated with hydrogen sulphide under press., is decolorized. G. Bellucci attributed the decolorization of soln. of litmus, indigo, etc., to the formation of colourless compounds with the sulphur of hydrogen sulphide. G. N. Guam and J. A. Wilkinson measured the conductivities of various substances dissolved in liquid hydrogen sulphide.

The sp. conductivities in mhos $\times10^7$ were for: hydrogen chloride (8·813), chlorine (1·787), bromine (1·614), iodine (136·000), iodine trichloride (13·420), mercuric bromide (51·6), mercuric iodide (99·9), mercuric chloride (0·31), zinc chloride (6·34), silicon tetrachloride (1·29), ferric chloride (20·99), sulphur monochloride (10·340), phosphorus trichloride (0·4254), phosphorus tribromide (0·5269), arsenic trichloride (11·510), antimony trichloride (4244·000), stannic chloride (1·680), thiocarbanilide (9·610), acetic acid—0·1 mol.—(nil), acetic acid—0·1 mol., room temp.—(0·634), acetic anhydride (41·260), thioacetic acid (2·960), acetyl chloride (18·800), and acetoamide (1·680). The following did not form conducting soln.: potassium, strontium, barium, cadmium, chromic (green and violet), manganous, and cobalt chlorides, potassium and ammonium hydrosulphides, bismuth trichloride, carbon disulphide, *n*-butyl sulphide, *n*-butyl mercaptan, thiophenol, *p*-thiocresol, thionaphthol, chloroform, bromoform, iodoform, trichloroacetic acid, benzoic acid, dinitrobenzene, stearic acid, and palmitic acid.

J. F. Daniell, and W. Beetz compared the electromotive force of elements with carbon or platinum, or palladium sat. with hydrogen sulphide in dil. sulphuric acid as the anode, and the simple element as cathode. For $Pd_{H_2S} \mid H_2SO_4 \mid Pd_2$, J. F. Daniell found 0·41 volt; and for $C_{H_2S} \mid H_2SO_4 \mid C$, 0·29 volt. W. Beetz made observations on this subject. N. Isgarischew and E. Koldaewa discussed the poisoning of the H-electrode by hydrogen sulphide, arsenic trioxide, etc. D. F. Smith and J. E. Mayer found for the **reduction potential** and decrease of free energy for $S+2H^{\cdot}=H_2S$ at 25° respectively —0·141 volt, and —6400 cals.; for $SO_2+6H^{\cdot}=H_2S+2H_2O$, respectively —0·360 volt, and —49,840 cals.; and for $SO_4''+10H^{\cdot}=H_2S+4H_2O$, respectively —0·304 volt, and —56,190 cals. According to J. Garnier, in the electrolysis of molten sulphides, out of contact with air, with a carbon anode, the sulphur reacts with the carbon, forming carbon disulphide.

H. S. Blackmore made some observations on this subject. According to M. Merle, and A. Scheurer-Kestner, when a soln. of sodium sulphide is electrolyzed, the sulphide is oxidized to sulphate; and F. W. Durkee said that thiosulphate is formed as an intermediate stage of the oxidation, but A. Scheurer-Kestner did not accept this result. E. F. Smith also studied the oxidation of the sulphides by electrolysis. W. Skey found that if the sulphides of silver, gold, mercury, lead, and platinum be employed as anodes they are reduced to the metal with the evolution of hydrogen sulphide. According to I. Bernfeld, in the electrolysis with electrodes of metallic sulphides, the following changes occur. (1) In acid soln.: at the anode, the metal is dissolved and the sulphur precipitated or oxidized; at the cathode, hydrogen sulphide is formed with separation of the metal; (2) in alkaline soln.: at the anode, the metal forms a hydroxide and the sulphur is oxidized; at the cathode, the metal is precipitated and the sulphur passes into soln. as an ion. According to F. Hund, the distance apart of unlike ions for the HS′-ion is $1·5\times10^{-8}$ cm., and for H_2S, $1·5\times10^{-8}$ cm.; the distance apart of like ions is for the H_2S, $1·6\times10^{-8}$ cm., and for the energy of complete separation of one hydrogen nucleus from the HS′-ion is 430 Cals., and for H_2S, 310 Cals. W. T. Skilling found a soln. of potassium chloride in liquid hydrogen sulphide to be non-conducting. B. D. Steele and co-workers found that although hydrogen chloride and bromide readily dissolve in liquid hydrogen sulphide, the soln. are non-conducting. They also measured the conductivity of soln. of triethylammonium chloride, tetramethylammonium chloride, nicotine, and of piperidine in liquid hydrogen sulphide. They also measured the raising of the b.p. by toluene, and triethylammonium chloride as solutes—the molecular raising of the b.p. is 620.

L. B. Loeb and A. M. Cravath found that the mobility of the positive ion in hydrogen sulphide is 0·61 cm. per sec. per volt per cm., and of the negative ion, 0·55 cm. per sec. per volt per cm. P. Eversheim found the **dielectric constant** of liquid hydrogen sulphide to be for $\lambda=\infty$, 5·93 at 10°; 4·92 at 50°; 3·76 at 90°; and 2·7 at the critical temp. H. J. von Braunmühl gave $0·69\times10^{-24}$ for the dielectric constant, and for the **electric moment,** $1·101\times10^{-18}$; C. T. Zahn and J. B. Miles gave $(\epsilon-1)vT=0·001223T+0·732$ for the dielectric constant of the purified gas when v is the sp. vol., and T, the absolute temp.; and $0·931\times10^{-18}$ for the electric moment. K. Honda and K. Otsuka found the **sparking voltage** of 56 to be necessary with tubular electrodes, 10 cms. apart, using a 50-cycle alternating current.

The chemical properties of hydrogen sulphide.—Dry hydrogen sulphide is decomposed by exposure to **light**: $H_2S=H_2+n^{-1}S_n$. The reaction is endothermal, and the wave-length of the active radiation is 2300 A. to 1800 A. The reaction was discussed by V. Henri,[19] D. Berthelot and H. Gaudechon, A. Smits and A. H. W. Aten, H. Tramm, and R. H. Gerke. E. Böhm and K. F. Bonhöffer[20] found that active **hydrogen** is de-activated by hydrogen sulphide, and quantities over one per cent. repress the Balmer spectrum of hydrogen. M. Scanavy-Grigorieva found that when hydrogen is passed over platinum, palladium, copper, and glazed porcelain, at 600° to 700° hydrogen sulphide is formed, presumably owing to the presence of sulphur adsorbed from the atmosphere. Hence, many proofs of the activation of hydrogen after its passage over glowing metals by showing that it forms hydrogen sulphur, are invalidated. A. G. White studied the limits for the propagation of flame in mixtures of hydrogen and hydrogen sulphide. According to H. Davy, hydrogen sulphide burns in **air** or **oxygen** under conditions similar to those for hydrogen. It is ignited by charcoal or iron at a low red-heat. According to J. Dalton, hydrogen sulphide burns in air with a blue flame, forming water and sulphur dioxide and depositing sulphur. A. Smithells and H. Ingle analyzed the flame into two cones, and found that most of the sulphur escapes from the first cone without undergoing combustion. When mixed with oxygen, hydrogen sulphide explodes on ignition. One vol. of hydrogen sulphide exploded with half a vol. of oxygen forms water and sulphur; and with 1·5 vols. of oxygen, it forms water and sulphur dioxide. A. Pedler represented the reaction with sufficient air or oxygen: $2H_2S+3O_2=2H_2O+2SO_2$; and with a deficiency of oxygen: $2H_2S+O_2=2H_2O+2S$. This preferential combustion of the hydrogen at the expense of the sulphur was applied by C. F. Claus to the recovery of sulphur from the by-products of the black-ash process of making soda; and, according to J. Habermann, is the primary cause of the occurrence of sulphur in volcanic districts. G. W. Jones and co-workers discussed the explosibility of mixtures of hydrogen sulphide and air; and D. S. Chamberlin and D. R. Clarke, the speed of the flame of the burning gas. R. Piria found that if a stream of hydrogen sulphide be sent through an inverted flask with the bottom removed, so that a mixture of air and hydrogen sulphide is formed, the mixture is inflamed by contact with red-hot coal, etc., and burns, forming a thick cloud of water, sulphur dioxide, and sulphur resembling the fumes ejected from the fumaroles of Agnano (Naples). According to F. Freyer and V. Meyer, the ignition temp. of a mixture of hydrogen sulphide with three times its vol. of oxygen streaming into air is 315°–320°; and when heated in a closed vessel to 250°–270°, an explosion occurs. J. W. Döbereiner found that spongy platinum does not ignite a mixture of oxygen and hydrogen sulphide, but it does so if hydrogen be also present, and A. de la Rive and F. Marcet showed that palladiumized or platinized paper-ash must be heated to 100° before it will become red-hot in a stream of hydrogen sulphide. It may then set the gas on fire. T. Graham found that a ball of platinized clay causes the slow oxidation of hydrogen sulphide admixed with oxygen; water is formed, and sulphur is deposited on the platinized clay. If a mixture of equal vols. of hydrogen, oxygen, and hydrogen sulphide be similarly treated, only the hydrogen of the hydrogen sulphide is oxidized during the first 24 hrs.; only afterwards does the free hydrogen unite with the oxygen. According to E. Carstanjen the gas is ignited by thallium trioxide; and, according to R. Böttger, by manganese, lead, or silver peroxide, or by chlorates or chromates; barium dioxide; or by silver, copper, or nickel oxide, and many silver and mercury salts only inflame the gas when heated. F. Bayer and Co. used porous silicic acid as catalyst for the reaction between oxygen and hydrogen sulphide. According to J. B. A. Dumas, sulphuric acid is formed when hydrogen sulphide is slowly oxidized in air. The presence of moisture is necessary for the oxidation. C. J. St. C. Deville observed that a mixture of hydrogen sulphide, steam and air, corresponding with many fumarole gases, when allowed to act for some months on broken fragments of rocks, forms sulphates of the alkalies and alkaline earths. According to J. B. A. Dumas, the formation of sulphuric acid by the oxidation of moist hydrogen sulphide can be observed at the baths of Aix (Savoy), for the limestone walls are soon covered with crystals of gypsum; and iron hooks, with green crystals of ferrous sulphate—yet the gas is itself free from sulphuric acid. Similarly, the fumarole gases of Tuscany, free from sulphuric acid, convert the lime of soil into gypsum. The waters of the Rio de Pasambio (South America) were found by A. von Humboldt and J. B. J. D. Boussingault to contain sulphuric acid derived from the oxidation of the hydrogen sulphide from the adjacent volcano of Purace. U. Bresciani found that in steam at 120° hydrogen sulphide is incompletely oxidized to sulphuric acid by a large excess of ozonized oxygen. R. Nitzschmann and E. Vogel discussed the oxidation of hydrogen sulphide to sulphurous acid.

An aq. soln. of hydrogen sulphide was found by L. N. Vauquelin to be slowly oxidized by exposure to air, forming water and milk of sulphur, as well as some sulphuric acid. C. Herzog said that some ammonium sulphate was formed in a closed flask containing air, and an aq. soln. of hydrogen sulphide, but this has not been verified. E. Filhol said that no sulphuric acid is formed at all, but if sufficient alkali-lye be present to form sodium hydrosulphide, the oxidation occurs more slowly, forming sulphur, and alkali polysulphide and sulphate. J. Raab said that light favours the action; and M. Salazar and H. Newmann, that the aq. soln. decomposes more slowly in darkness than in light. C. F. Mohr preserved the soln. by covering it with a layer of petroleum to keep away the oxygen; and P. H. Lepage,

J. Raab, M. Salazar and H. Newmann, and A. J. Shilton said that the aq. soln. can be kept for a longer time without decomposition if glycerol be also present. D. Lindo said that the soln. in glycerol is no more stable than the soln. in water. A. J. Shilton reported that the presence of sugar or salicylic acid acts as a preservative. According to P. de Clermont and H. Guiot, dry oxygen does not act on the metal sulphides at ordinary temp., but many of them are transformed by moist air or oxygen into sulphates—*e.g.* ferrous sulphide. If the precipitated sulphides of manganese, iron, or nickel be strongly compressed, and exposed to moist air, they become heated owing to rapid oxidation; the sulphides of copper, zinc, and cobalt are oxidized more slowly, and no evolution of heat can be detected. H. A. Krebs observed that the rate of oxidation of aq. soln. of hydrogen sulphide or of alkali sulphides is greatly accelerated by the presence of a minute proportion of a heavy metal sulphide. For aq. soln. of hydrogen sulphide, nickel sulphide is the most active catalyst; for soln. of the gas in N-HCl, a mixture of manganese and iron sulphides is the most active. The so-called autoxidation of soln. of sulphides is attributed to the presence of traces of heavy metal sulphides. F. O. Smith and co-workers found that ultrasonic radiations on an aq. soln. of hydrogen sulphide form colloidal sulphur.

According to A. Desgrez and co-workers, free hydrogen sulphide may be removed from soln. by bubbling through them an inert gas like hydrogen or nitrogen. The free gas is removed from simple aq. soln. very quickly; with soln. to which sufficient sodium hydroxide has been added to produce the hydrosulphide, the gas is evolved more slowly as the result of the hydrolysis: $NaHS+H_2O=NaOH+H_2S$; and with sodium sulphide in soln. the decomposition proceeds at a still slower rate, the first stage of the reaction is: $Na_2S+H_2O=NaOH+NaHS$. The rate of evolution of the gas is modified by the presence of certain salts. Sodium hydrocarbonate accelerates the removal of the gas; and potassium monophosphate still more so; whilst sodium borate has a smaller influence. Using buffer soln. of borate and phosphate, the rate of removal of hydrogen sulphide was found to depend on the p_H value, *i.e.* on the acidity of the liquid. Acidic soln. are unstable; alkaline soln., stable. There is a rapid transition at $p_H=8$ or 9. The mean p_H value of urine is 6·5, and this is taken to explain the absence of hydrogen sulphide from urine after considerable quantities of sulphuretted waters have been drunk. If an aq. soln. of hydrogen sulphide be heated in a sealed tube, at 200°, C. Geitner found that a blue liquid is produced on which float globules of sulphur. The liquid is decolorized on cooling, and it then becomes turbid owing to the separation of sulphur. The liquid contains some sulphuric acid. According to A. Gautier, on passing a current of hydrogen sulphide, saturated with water vapour at 100°, through a red-hot tube provided with a condenser, sulphurous acid, sulphuric acid in small quantity, and colloidal and precipitated sulphur collect in the latter, and hydrogen is also evolved.

C. F. Schönbein, and W. Helbig said that **ozone** oxidizes the gas or the aq. soln. of hydrogen sulphide to sulphur and water. A. Mailfert also observed that ozone converts the sulphides of the alkalies, alkaline earths, copper, zinc, cadmium, and antimony into sulphates; cobalt and nickel sulphides, first into sulphates, and then into sulphuric acid and peroxide; gold sulphide, into gold and sulphuric acid; silver, bismuth, and platinum sulphides into sulphuric acid; manganese, lead, and palladium sulphides into sulphuric acid and peroxide; while mercuric sulphide is but slowly attacked. H. C. Jacobsen discussed the oxidation of hydrogen sulphide to sulphuric acid by bacteria—*vide supra.*

Early observations on the solubility of hydrogen sulphide in **water** were made by W. Henry,[21] who found that one vol. of water absorbs 1·08 vols. of gas at 10°; N. T. de Saussure, 2·53 vols. at 15°; J. L. Gay Lussac and L. J. Thénard, 3 vols. at 11°; T. Thomson, 3·66 vols. at ordinary temp.; and J. Dalton, 2·5 vols. at ordinary temp. R. de Forcrand and P. Villard gave 4 vols. at 0° and ordinary press., and 100 vols. at 0° and 820 mm. press., while F. Pollitzer found that a litre of water dissolves 0·1004 mol. H_2S at 25° and 760 mm. L. Carius found that one vol. of water at θ° absorbs S vols. of hydrogen sulphide reduced to 0°—760 mm. press.:

	0°	5°	10°	15°	20°	25°	30°	35°	40°
S .	4·3706	3·9652	3·5858	3·2326	2·9053	2·6091	2·3290	2·0799	1·8569

R. Bunsen and E. Schönfeld represented the results by the formula $S=4{\cdot}3706-0{\cdot}083687\theta+0{\cdot}0005213\theta^2$; and F. Henrich, $S=4{\cdot}4015-0{\cdot}89117\theta+0{\cdot}00061954\theta^2$—*vide infra*. L. W. Winkler represented the coeff. of absorption—*i.e.* the vol. of gas reduced to 0° and 760 mm. which is absorbed by one vol. of liquid when the press. of the gas itself, without the partial press. of the solvent, is 760 mm.—at 0° by 4·6210; at 20°, by 2·554; at 40°, by 1·642; and at 60°, by 1·176. G. Fauser gave 4·686 at 0°, and 2·672 at 20°. P. K. Prytz and H. Holst gave 4·6796 at 0°; and F. Henrich, 4·4015 at 0°, and at

	2°	9·8°	14·8°	19°	23°	27·8°	35·6°	43·3°
S .	4·2373	3·5446	3·2651	2·9050	2·7415	2·3735	1·9972	1·7142

E. P. Perman measured the rate of escape of hydrogen sulphide from its aq. soln.; and W. H. McLauchlan showed that the gas is less soluble in a soln. of sodium or calcium chloride than in water. They also found that the solubility of hydrogen sulphide in water follows Henry's law—**1.** 10, 4—that the solubility in salt soln. is lowered in the following way:

The vol. of hydrogen sulphide absorbed by one vol. of aq. soln. at 25° is 2·61 for N-NH_4Br; 2·40, for N-NH_4Cl; 2·58, for N-NH_4NO_3; 2·14, for 0·5N-$(NH_4)_2SO_4$; 2·37, for 0·25N-$(NH_4)_2SO_4$; 2·47, for N-KBr; 2·22, for N-KCl; 2·38, for N-KNO_3; 2·04, for 0·5N-K_2SO_4; 2·32, for 0·25N-K_2SO_4; 2·56, for N-KI; 2·44, for N-NaBr; 2·21, for N-NaCl; 2·42, for 0·5N-NaCl; 2·32, for N-$NaNO_3$; 1·90, for 0·5N-Na_2SO_4; and 2·32, for 0·25N-Na_2SO_4. L. Dede and T. Becker found that neutral soln. of the following salts dissolved the following number of grams of hydrogen sulphide per 100 c.c. of soln.:

	0	1	2	4
$CaCl_2$ . . .	0·392	0·350	0·313	0·270
$NaClO_4$ . . .	0·392	0·340	0·293	0·220
Na_2SO_4 . . .	0·392	0·348	0·306	0·257

F. L. Crobaugh found that the gas is soluble in an aq. soln. of ammonium cadmium chloride. According to H. Goldschmidt and H. Larsen, a litre of 0·05N-NaSH dissolves 0·082 and 0·064 mol of hydrogen sulphide respectively at 35° and 45°; a litre of 0·1N-NaSH dissolves 0·132, 0·104, and 0·082 mol of hydrogen sulphide respectively at 15°, 25°, and 35°; and a litre of 0·2N-NaSH at 15° and 25° dissolves respectively 0·129 and 0·1035 mol of hydrogen sulphide.

According to F. Wöhler, when moist hydrogen persulphide is enclosed in a sealed tube, it decomposes into sulphur and hydrogen sulphide along with a few transparent, colourless crystals, which, on opening the tube, immediately liquefy and volatilize. They are supposed to be **hydrated hydrogen sulphide.** Again, if hydrogen sulphide be passed through alcohol mixed with enough water so that the mixture does not freeze at —18°, octahedral crystals are produced resembling ice. The crystals quickly disappear, with brisk effervescence, when removed from the freezing mixture; if enclosed in a sealed tube, they disappear at ordinary temp. but reappear when the tube is cooled down to —18°. R. de Forcrand obtained a hydrate of hydrogen sulphide by compressing hydrogen sulphide in contact with water. There is a difficulty in determining the proportion of water in the hydrate; in 1882, R. de Forcrand estimated indirectly that the hydrate was $H_2S.15H_2O$; in 1883, he gave $H_2S.12H_2O$; in 1888, R. de Forcrand and P. Villard gave $H_2S.7H_2O$; in 1911, F. E. C. Scheffer, $H_2S.5H_2O$; and in 1925, G. N. Quam, $H_2S.6H_2O$. P. Villard argued by analogy with other gas hydrates that the formula should be $H_2S.6H_2O$; he found that the liquid crystallized when seeded with the hydrate $N_2O.6H_2O$, and this makes the formula $H_2S.6H_2O$ probable. R. de Forcrand, in 1902, found that, as a rule, when the 3-phase line of a dissociating compound which splits up into a solid and a gas reaches a vap. press. of one atm., the quotient of the heat of transformation and the absolute temp. approximates 30. The rule conforms with the formula $H_2S.6H_2O$ for this hydrate, but fails with $SO_2.8H_2O$. F. E. C. Scheffer and G. Meijer also showed that the assumption that the compound is **hexahydrated hydrogen sulphide,** $H_2S.6H_2O$, best explains the behaviour of the hydrate under varying conditions of temp. and press.

The soln. of hydrogen sulphide and water separates into two layers, expressing the composition in mols of hydrogen sulphide per 100 mols of water. F. E. C. Scheffer found

	0°	6°	17°	26°	29·5°	29·4°	26·9°	22·9°	13·7°	5·3°
H_2S .	0·4	0·5	0·8	1·2	1·6	96·3	97·3	98·2	99·1	99·5
	L_1—Layer rich in H_2S					L_2—Layer rich in H_2O				

The 2-phase lines *OB* (solid and vapour), *BL* (liquid and vapour), and *BC* (solid and liquid), Fig. 35, represent the ordinary equilibrium diagram of the hexahydrate; the line *BC* refers to the system containing the hydrate, liquid-2, and vapour. The 3-phase line *FC*, Fig. 35, represents the solid hydrate, solid water, and the vapour of ice and hydrogen sulphide: $H_2S.6H_2O_{solid} \rightleftharpoons 6H_2O_{solid} + H_2S_{gas}$:

θ . .	−25·85°	−19·75°	−15·8°	−11·85°	−7·95°	−4·95°	−2·4°
p . .	22·35	30·2	36·2	43·3	51·5	58·6	65·5

The equation of the line *FC* is $\log p = -1333T^{-1} + 6{\cdot}7393$. The 3-phase line *CD* represents the solid hydrate, liquid water, and vapour: $H_2S.6H_2O_{solid} \rightleftharpoons 6H_2O_{liquid} + H_2S_{gas}$; *GD* refers to the hydrate, liquid-1, and vapour; *CH*, to the solid hydrate, ice, and liquid-2; *DJ*, to the solid hydrate, and the two liquids; and *DK*, to the two liquids and vapour. The quadruple point *C*, at 0·4° and 700 mm. press., has solid hydrate, ice, liquid-2, and vapour in equilibrium; and the quadruple point *D*, at 29·5° and 22·1 atm., has the solid hydrate, the two liquids, and vapour in equilibrium. The thermal value of the reaction is $H_2S.6H_2O_{solid} = H_2S_{gas} + 6H_2O_{solid} - 5{\cdot}550$ Cals. and of $H_2S.6H_2O_{solid} = H_2S_{gas} + 6H_2O_{liquid} - 14{\cdot}270$ Cals. R. de Forcrand and H. Fonzes-Diacon gave for the heat of formation of the solid hydrate: $(H_2S_{gas}, nH_2O_{liquid}) = 16{\cdot}34$ Cals. R. de Forcrand and P. Villard said that the temp. of formation of the crystals of the hydrate at different press., p mm., are:

	0°	1°	2·1°	3·4°	5·2°	19·8°	28·5°
p . .	731	820	907	1048	1250	5396	12,160

L. P. Cailletet and L. Bordet also measured the temp. of formation at different press., and found at 1·0°, 2 atm.; at 14°, 5·4 atm.; and at 25°, 16 atm.; and they gave 29° for the critical temp. of existence, while R. de Forcrand gave 30°.

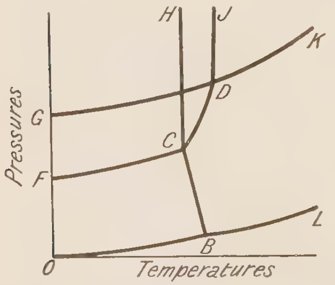

FIG. 35.—Diagrammatic Representation of the Effect of Temperature and Pressure on Hydrated Hydrogen Sulphide.

According to L. J. Thénard,[22] hydrogen sulphide, or its aq. soln., is decomposed by **hydrogen dioxide,** forming sulphur and water, and, added A. Classen and O. Bauer, the reaction $H_2O_2 + H_2S = S + 2H_2O$ does not take place in the presence of ammonia or potassium hydroxide, for then sulphuric acid is produced. According to C. Zenghelis and S. Horsch, when hydrogen sulphide is passed over **sodium dioxide,** a very vigorous action occurs either in the presence or the absence of air, and if the dioxide is previously warmed, the action is accompanied by a flame and the containing vessel of glass or porcelain is attacked. The products of the action vary according to the conditions. The hydrogen of the hydrogen sulphide always goes to form water, which in its turn partly attacks the hydrogen dioxide. In the absence of air the sulphur forms sodium sulphide and polysulphides, together with a small amount of thiosulphate and sulphate, and if the current of hydrogen sulphide is rapid there is a deposition of a small amount of free sulphur. In the presence of air scarcely any sulphide is formed, but sodium sulphate and free sulphur are obtained. If the containing vessel is attacked owing to a very vigorous action, then the solid products have a blue tinge, due to the iron in the glass or porcelain. M. V. N. Swamy and V. Simhachelam found that with 98·6 per cent. **lead dioxide,** hydrogen sulphide, diluted with 5 vols. of air, does not react below 2·5 atm. press., but the dark brown colour becomes light red; with 87·7 per cent. lead dioxide there is a reaction with hydrogen sulphide diluted with 15 vols. of air.

According to H. Moissan, **fluorine** inflames in contact with hydrogen sulphide, forming hydrogen fluoride and sulphur hexachloride. A. Stock observed that at −100°, **chlorine** reacts with hydrogen sulphide dissolved in liquid hydrogen chloride to form sulphur; no evidence of the existence of a *sulphur hydrochloride*, SHCl, was observed. H. Rose said that chlorine, **bromine,** and **iodine** when warmed with hydrogen sulphide form sulphur and the respective hydrogen halide: $H_2S+I_2=2HI+S$; and if the halogen is in excess, the sulphur may form sulphur halide, and some sulphuric acid. A. Naumann explained the different effects by the thermochemical data: $Br_2+H_2S=2HBr+S+15{\cdot}5$ Cals., and with an excess of water the hydrogen bromide reacts evolving 40 Cals. of heat; with iodine in place of bromine, the thermal effects are respectively 16·5 Cals. and 39 Cals. Iodine does not react with hydrogen sulphide alone; indeed, M. Berthelot observed no reaction when the two substances are heated in a sealed tube at 500°. In the presence of water, hydriodic acid is formed up to a certain value limited by the reverse reaction between sulphur and the halogen acid. A. Naumann said that iodine and hydrogen sulphide can react on each other only in the presence of water until, by the increasing amount of hydriodic acid in the water, the positive amount of the heat of absorption of the hydriodic acid has fallen from 39·0 Cals. to 16·5 Cals. M. Berthelot suggested that the limited action is due to the formation of a definite hydrate, $HI.7H_2O$, but there is no evidence of the formation of any such compound. For the reversible reaction $2HI_{gas}+2S_{solid}\rightleftharpoons 2I_{solid}+H_2S_{gas}$, if the bracketed symbols denote partial press., $[HI]^2=K[H^2S]$, where $K=1{\cdot}9\times10^{-3}$ at 40·1°; 45×10^{-3} at 50·1°; $9{\cdot}96\times10^{-3}$ at 60·2°; and 47×10^{-3} at 80·7°. The thermal value of the reaction is 16·8 Cals. at 50°; 17·35 Cals. at 60°; 17·12 Cals. at 60°; 17·70 Cals. at 80°. L. B. Parsons found that the reaction between hydrogen sulphide and iodine is complete in absence of water and incomplete in presence of water, the equilibrium point reached depending on the water content of the solvent. In anhydrous ether, the reaction proceeds according to the equation: $H_2S+I_2=2HI+S$; and in the presence of water, a series of consecutive reactions occurs; these may be summed into a single equation: $H_2S+3H_2O+3I_2\rightleftharpoons H_2SO_3+6HI$. The changes in the course of the reaction in the presence of atmospheric oxygen are ascribed to the formation of ethyl peroxide which oxidizes hydriodic acid to iodine and water, but does not oxidize hydrogen sulphide. H. Heinrichs studied the reaction between iodine and hydrogen sulphide; and R. W. E. MacIvor, that between **iodine trichloride** and hydrogen sulphide. W. H. McLauchlan found that one vol. of 0·5*N*-**hydrochloric acid** at 25° dissolves 2·54 vols. of hydrogen sulphide. J. Kendall and J. C. Andrews gave for the solubility of hydrogen sulphide—*S* mols of H_2S per litre, or β vols. of H_2S reduced to 0° and 760 mm. per vol. of soln. under a press. of hydrogen sulphide of 760 mm.—in hydrochloric acid of normality *N*:

HCl .	0*N*-	0·1348*N*-	0·6308*N*-	1·848*N*-	2·498*N*-	3·308*N*-	4·410*N*-	4·874*N*-
β .	2·266	2·253	2·250	2·272	2·291	2·301	2·384	2·413
S .	0·1023	0·1018	0·1016	0·1026	0·1034	0·1039	0·1076	0·1090

G. Baume and N. Georgitses measured the f.p. of the system: liquid **hydrogen chloride** and liquid hydrogen sulphide, and the results are indicated in Fig. 36. The curve is characteristic of that for solid soln., with a minimum at −117·5°. K. Jellinek and co-workers studied the heterogeneous equilibria with hydrogen sulphide and **metal chlorides**—silver, cadmium, and manganese. L. S. Bagster obtained a curve analogous with that of hydrogen chloride, Fig. 36, for liquid **hydrogen bromide** and hydrogen sulphide, Fig. 36, with a minimum at −88° with 48·5 molar per cent. of hydrogen bromide; and also for **hydrogen iodide** and hydrogen sulphide, Fig. 36, with a minimum at about −90·8° with 28·4 molar per cent. of hydrogen iodide. Expressing concentrations in mols per litre, F. Pollitzer found the solubility of hydrogen sulphide in soln. of **hydriodic acid** at 25° and 760 mm., to be:

HI .	0	1·01	1·93	2·64	4·38	5·005	5·695	6·935	(9·21)
H_2S .	0·1004	0·111	1·125	0·138	0·163	0·165	0·181	0·197	(0·267)

A. J. Balard found that hydrogen sulphide inflames in contact with **chlorine monoxide.** G. Lunge and G. Billitz observed that an aq. soln. of hydrogen sulphide is oxidized by **hypochlorous acid** to water, sulphuric acid, hydrochloric acid, and chlorine. T. L. Phipson said that if a stream of hydrogen sulphide be directed on to a piece of **calcium hypochlorite,** heat is generated, and the hydrogen and a large part of the sulphur burn at the cost of the oxygen of the hypochlorite, and chlorine is set free. W. Feit and C. Kubierschky found that a soln. of hydrogen sulphide is oxidized by **iodic acid,** forming water, sulphur, and iodine; **bromic acid** forms water, sulphur, and bromine; **alkali iodates** yield water, sulphur, sulphuric acid, and iodine; and G. Lunge and G. Billitz found that **alkali bromates** yield water, sulphur, sulphuric acid, and bromine.

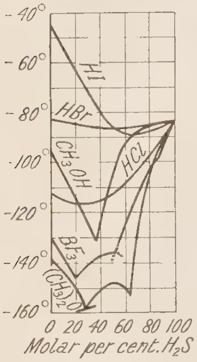

FIG. 36.—Freezing-point Curves with Binary Systems containing Hydrogen Sulphide.

According to J. Dalton,[23] one vol. of **sulphur dioxide** reacts with 2 vols. of hydrogen sulphide, at ordinary temp., forming water, and sulphur—along with some pentathionic acid. T. Thomson regarded the mixture as a sulphite of hydrogen sulphide. M. Cluzel, and W. Schmid found that the dried gases do not react, but they do so immediately a trace of water is introduced into the system. From their study of the reverse reaction, G. N. Lewis and M. Randall calculated for the reaction at constant press., $2H_2S+SO_2=3S_{liq.}+2H_2O+Q$ cals., $K_p=p^2{}_{H_2O}p^{\frac{1}{2}}{}_{S_6}/p^2{}_{H_2S}p{}_{O_2}=649$; and $Q=25{,}719$ cals. H. A. Taylor and W. A. Wesley measured the velocity of the reaction between sulphur dioxide and hydrogen sulphide, and found that the velocity of the reaction is proportional to the surface area of the reacting chamber, and the velocity V can be represented by $V=KS^2{}_{H_2S}S_{SO_2}$, where S denotes the fraction of the surface covered by the mols. of the respective gases. Since $s=kp^{1/n}$ for each gas, $V=k'p^{2/n}_{H_2S}p^{1/m}_{SO_2}$, when $n=\frac{4}{3}$, and $m=1$. The velocity at a constant temp. varies directly as the partial press. of the sulphur dioxide, and as the partial press. of the hydrogen sulphide raised to the 1·5th power. The glass surface hence acts as a contact catalyst; and it is assumed that each of the reacting gases is activated by adsorption on the surface of the glass, and the reaction then follows between the activated molecules. G. N. Quam said that dry sulphur dioxide reacts vigorously with liquid hydrogen sulphide. W. Biltz and M. Bräutigam represented the f.p. of the binary system: H_2S–SO_2 by Fig. 37. W. R. Lang and C. M. Carson represented the first reaction with the gases in $2H_2S+SO_2=3S+2H_2O$; and observed that with the liquids there is a slow formation of sulphur; and H. B. Baker

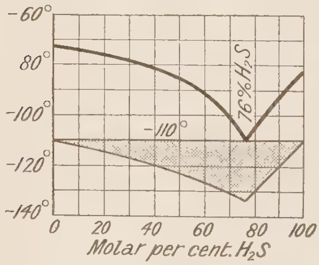

FIG. 37.—Freezing-point Curve of the System: SO_2–H_2S.

found that liquid alcohol, and liquid sulphur dioxide can liberate sulphur from the dried mixed gases, whereas carbon tetrachloride is inert. According to D. Klein, immediate action is produced by water, ethyl alcohol, *iso*butyl alcohol, *iso*amyl alcohol, acetone, propyl acetate, benzaldehyde, and carvone. A slower decomposition occurs with methyl ethyl ketone, acetonitrile, propionitrile, valeronitrile, phenylacetonitrile, methyl benzoate, *iso*butyl acetate, and ethyl ether. On the other hand, carbon disulphide, acetyl chloride, benzoyl chloride, ethyl chloride, and carbon tetrachloride are quite inert. There appears to be no connection between the dielectric capacity or association factor of a liquid and its activity as a catalyst in this reaction. Many of the active liquids are known to form compounds with hydrogen sulphide, notably the nitriles, the aldehydes, and carvone. E. Matthews also found that in order to bring about the decomposition of a mixture of sulphur dioxide and hydrogen sulphide in either the gaseous or the liquid state, the addition of a third substance in the liquid phase is necessary. There is no rigid relationship between the values of the dielectric constants of substances and their chemical activity as measured by their ability to bring about the interaction of hydrogen sulphide and sulphur dioxide. Hydrogen sulphide and sulphur dioxide when in liquid state do not react vigorously. The activity of a substance in causing decomposition is dependent on the solubility of the two gases in the substance when liquid, or on the solubility of the solids in the liquid mixture of the two gases. E. Mulder showed that above 400°, both gases can exist besides one another in the presence of steam: $2H_2S+SO_2\rightleftharpoons 3S_{vapour}+2H_2O_{gas}$—*vide supra*, the preparation and formation of sulphur. The interaction of hydrogen sulphide and sulphurous acid was also discussed by H. W. F. Wackenroder, H. Debus, W. R. Lang and C. M. Carson, etc., in connection with the polythionic acids—*vide supra*—H. Debus supposed that the first reaction results in the formation of tetrathionic acid, and that the other thionic acids are formed by secondary reactions. I. Guareschi arranged the experiment to give the sulphur in the form of vortex rings. A. Geuther observed that hydrogen sulphide is immediately decomposed by conc. **sulphuric acid,** forming water, sulphur dioxide, and sulphur which dissolves in the acid, forming a blue liquid. J. W. Döbereiner obtained a similar result with furnishing sulphuric acid; and A. Vogel, with rectified sulphuric acid, and slowly with a 1 : 4-mixture of sulphuric acid when impurities—like sulphurous and arsenious acids—are present. W. H. McLauchlan said that one vol. of $0{\cdot}5N\text{-}H_2SO_4$ dissolves 2·36 vols. of the gas at 25°. H. Prinz found that hydrogen sulphide does not react in the cold with **thionyl chloride,** but at 60°, hydrogen chloride, sulphur dioxide, and sulphur are formed. A. Besson said that the reaction occurs at ordinary temp. with the dried gases: $2SOCl_2+2H_2S=4HCl+SO_2+3S$; and, at higher temp., the main reaction is: $2SOCl_2+H_2S=S_2Cl_2+SO_2+2HCl$; while with dried **sulphuryl chloride** and hydrogen sulphide at ordinary temp., the reactions are: $SO_2Cl_2+H_2S=2HCl+SO_2+S$; and $SO_2Cl_2+2H_2S=2H_2O+S_2Cl_2+S$. H. Prinz found that hydrogen sulphide reacts in the cold with **chlorosulphonic acid** with the separation of sulphur and the evolution of hydrogen chloride—when the mixture is distilled, sulphur monochloride and sulphur trioxide collect in the receiver. According to W. Feit and C. Kubierschky, A. Gutbier and J. Lohmann, with **selenium dioxide,** water and selenium sulphide are formed.

F. E. C. Scheffer [24] has studied the binary system, **ammonia** and hydrogen sulphide; when the components are in molar proportions, the maximum sublimation point is 88·4° at 19 atm. press.; and the minimum m.p. is at 116°–117°, and 150 atm. The action on aq. ammonia, where the aq. soln. of hydrogen sulphide acts as an acid, has been previously discussed—**2.** 20, 42. According to F. Ephraim and H. Piotrowsky, hydrogen sulphide readily dissolves in **hydrazine hydrate,** but no solid is obtained. With anhydrous hydrazine, however, a crystalline compound is obtained in the form of long needles. More hydrogen sulphide is absorbed than corresponds with the formula $2N_2H_4,H_2S$, but not enough for the formula N_2H_4,H_2S. It is probable that the latter compound is formed, and by surrounding part of the hydrazine prevents further absorption of hydrogen sulphide. The compound readily loses hydrogen sulphide on exposure to the atmosphere, becoming liquid on account of the liberation of hydrazine. Its vapour tension was found to be 760 mm. at about 35°. According to C. Leconte, a mixture of dry hydrogen sulphide and dry **nitric oxide** does not react, but S. Cooke found that a mixture of the two gases explodes on the passage of an electric spark. The reaction was studied by J. A. Pierce. Fuming **nitric acid** vigorously attacks hydrogen sulphide, and, as shown by F. Kessel, A. W. Hofmann, and P. T. Austen, hydrogen sulphide burns with a yellow flame in the vapour of nitric acid, forming white fumes thought to be nitrosylsulphonic acid. A. Vogel, and N. A. E. Millon said that hydrogen sulphide has no action on nitric acid freed from nitrogen picroxide; and R. Kemper found that purified nitric acid of sp. gr. 1·8 does not act on hydrogen sulphide, but if the smallest trace of nitrogen peroxide is present—as is the case with nitric acid which has stood exposed to air—the sulphide is completely decomposed. J. W. F. Johnston, and C. Leconte observed that hydrogen sulphide reduces dil. nitric acid forming sulphur, sulphuric acid, ammonium sulphate, and nitric oxide. H. B. Dunnicliff and S. Mohammad added that 5 per cent. nitric acid is not attacked by hydrogen sulphide even in the presence of nitrous fumes. Soln. of higher conc., say 43 per cent. nitric acid, are attacked after a more or less long interval of time. This induction period is removed if nitrous fumes are introduced or slight decomposition of nitric acid is induced by insolation. The addition of sulphuric acid increases the induction period. A 43 per cent. soln. of nitric acid was used. The products of reaction are sulphuric acid, nitrous acid, ammonia, sulphur, nitric oxide, nitrous oxide, and nitrogen. A possible explanation of the evolution of nitrogen in the later stages is that ammonia is formed and immediately decomposed. If this is so, ammonia is not formed in the early stages of the reaction in any quantity though there is evidence to show that it might be formed later. Apparently the presence of sulphuric acid exerts considerable influence on the formation of nitrogen. There are, however, explanations for the existence of nitrogen other than through the agency of ammonia as an intermediate compound, and it is probable that any ammonia formed is the result of side reactions or minor secondary reactions. There is a concentration of ammonium salt below which there is no interaction with nitrous acid. The presence of sulphuric acid affects the progress and ultimate products of the reaction. If to the nitric acid, sulphuric acid is added before passing hydrogen sulphide, the reaction stops when the concentration of the nitric acid has fallen to 23 per cent. and the total sulphuric acid conc. is 15 per cent. These are roughly equivalent quantities, but isotonic soln. at lower conc. do not exhibit this stoppage in the progress of the reduction. It is probable that the nitric acid and sulphuric acid enter into a chemical combination which is inert to the action of hydrogen sulphide, but which at lower conc. become decomposed or dissociated and attackable by hydrogen sulphide. It is possible that the condition of stasis which occurs when the conc. of the nitric acid has fallen to 23 per cent., and that the conc. of the sulphuric acid has reached 15 per cent., may possibly be due to the combination of these two acids in soln. at these specified percentages which correspond very roughly with eq. quantities of the two acids, the nitric acid being slightly in excess. Salts of nitrato-sulphuric acid, HNO_3, H_2SO_4 or $(HO)_2{=}NO.OSO_2.OH$, *e.g.* $KNO_3,KHSO_4$ or HNO_3,K_2SO_4 and NH_4NO_3, corresponding with the constitution $(NH_4O).N(OH).O.SO_2.(ONH_4)$, have been obtained. It may be assumed that a compound $2HNO_3.H_2SO_4$, or $(HO)_2{=}NO.O.SO_2,O.NO{=}(OH)_2$, may be formed in soln., and that this compound does not react with hydrogen sulphide. According to G. Lunge and G. Billitz, nitric acid and some **nitrates** form with the aq. soln. of hydrogen sulphide, sulphur, sulphuric acid, nitric oxide, and ammonia; **aqua regia** forms sulphuric acid; and, according to M. Görlich and M. Wichmann, **nitrites** react with the aq. soln: $KNO_2+3H_2S=KOH+3S+NH_3+H_2O$, and if an excess of hydrogen sulphide be present, a hyposulphide is formed. L. S. Bagster found that the products of the reaction of a soln. of **nitrous**

acid with hydrogen sulphide vary with relative conc. With appreciable conc. of nitrous acid, the reduction products are chiefly nitric and nitrous oxides; with small conc. of nitrous acid, they are ammonia and hydroxylamine, the proportions of which vary according to the conc. of sulphide ion in soln. Nitric and nitrous oxides are regarded as products of hyponitrous acid formed primarily. The proportion of sulphur trioxide to free sulphur is small even with fairly conc. nitrous acid soln. unless the hydrogen sulphide conc. is small. Hydrogen sulphide reacts slowly with ammonium nitrite, converting it into ammonia. The rate of reaction is diminished by the addition of ammonium sulphide and increased by addition of polysulphide. It is suggested that the polysulphide ion is more acidic than the sulphide ion and would thus furnish a greater conc. of reducing ions in soln.

A. Colson found that although dry **silver phosphate and pyrophosphate** are not attacked by dry hydrogen sulphide at 0°, the action becomes distinct at 15° to 20°, and rapid at 100°. Dry **zinc phosphate** is not appreciably attacked between 5° and 9°, but the action becomes marked at 100°, and rapid at 160°. Experiments at 100° show that the mass of hydrogen sulphide decomposed by zinc phosphate in unit time and at a constant temp. is proportional to the square of the press. Dry **cupric phosphate** and orthophosphate, on the other hand, absorb hydrogen sulphide slowly but continuously at 0°. The rate of the reaction is greatly reduced if the press. is lowered, but is accelerated by a rise of temp. The decomposition of silver phosphate or pyrophosphate by hydrogen sulphide develops more heat than the decomposition of the corresponding cupric salts, and hence there seems to be no connection between the heat of decomposition and the temp. at which the reaction will take place. When dry hydrogen sulphide is brought in contact with silver phosphate, the gas is at first absorbed somewhat rapidly, then more slowly, and finally a condition of equilibrium is reached in about 3 days, the pressure of the residual gas being 125 mm. at 12°; the equilibrium is not appreciably affected by increasing the press. of the gas, but is at once disturbed by a rise of temp. At 109°, the reaction rapidly becomes complete. Similar phenomena were observed with silver pyrophosphate; the higher the temp., the greater the amount of change before equilibrium is established, and the lower the press. of the residual gas. The reaction between a chloride and a non-volatile acid is endothermic, and that between metallic salts and hydrogen sulphide is exothermic, but in both cases a rise of temp. promotes the reaction and a fall of temp. retards it. G. S. Sérullas observed that hydrogen sulphide reacts with **phosphorus trichloride,** forming hydrogen chloride and phosphorus trisulphide; while E. Baudrimont represented the reaction with **phosphorus pentabromide:** $H_2S+PBr_5=PSBr_3+2HBr$; and similarly with the reaction with **phosphorus pentachloride.** A. Besson found that **phosphoryl chloride** reacts with dry hydrogen sulphide at 0°, forming solid $P_2O_2S_3$; and at 100°, liquid $P_2O_2SCl_4$. J. Myers represented the reaction with **arsine:** $3H_2S+2AsH_3=As_2S_3+6H_2$. In air at ordinary temp., the arsine is first oxidized and the product is then converted to trisulphide; at 230°, in the absence of air, arsenic and arsenic sulphide are formed. O. Brunn found that with **stibine** hydrogen sulphide reacts in the absence of air and in darkness, forming antimony trisulphide; the reaction proceeds more quickly in light. Quinquevalent **vanadium salt** soln. are reduced to the quadrivalent state by hydrogen sulphide—*vide* vanadic acid.

H. Köhler [25] found that if a mixture of hydrogen sulphide and **carbon dioxide** be sent through a red-hot tube, the reaction can be symbolized: $CO_2+H_2S=S+CO+H_2O$, with the possible formation of carbonyl sulphide, discussed by R. Meyer and S. Schuster. A. Gautier represented the reaction: $8CO_2+9H_2S=3COS+5CO+H_2+8H_2O+6S$; and said that carbonyl sulphide has been noted by several observers in vlocanic gases, and in sulphuretted waters in volcanic neighbourhoods. The condensation of **acetylene** and hydrogen sulphide to form thiophen was studied by A. E. Tschitschibabin, W. Steinkopf and J. Herold, W. Steinkopf and G. Kirchhoff, V. Meyer and T. Sandmeyer, P. Sabatier and

A. Mailhe, and M. G. Tomkinson. The liquefaction of mixtures of sulphur dioxide and **ethane** was studied by W. Mund and P. Herrent; and the propagation of flame in mixtures of hydrogen sulphide with **methane** and with **carbon disulphide** by A. G. White. Hydrogen sulphide is soluble in carbon disulphide. W. Biltz and M. Bräutigam represented the f.p. of mixtures of carbon disulphide and hydrogen sulphide by the curve, Fig. 38. The **thiohydrated carbon disulphide,** $CS_2.H_2S$, may be a thiocarbonic acid, H_2CS_3; and the compound **hexathiohydrated carbon disulphide,** $CS_2.6H_2S$, corresponds with $CO_2.6H_2O$. The f.p. curve of mixtures of **carbon tetrachloride** and hydrogen sulphide is shown in Fig. 39. Hydrogen sulphide is soluble in **ethyl alcohol;** N. T. de Saussure found that 100 vols. of alcohol of sp. gr. 0·84 absorb 600 vols. of the gas; while L. Carius found that one vol. of alcohol at θ° and 760 mm. press. absorbs the following amounts of gas reduced to 0° and 760 mm.:

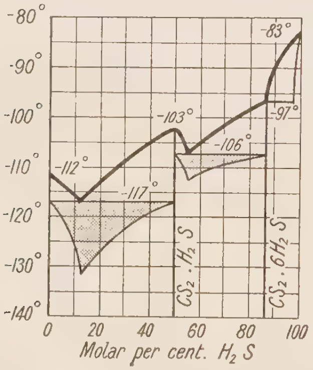

FIG. 38.—Freezing-point Curves in the System: H_2S–CS_2.

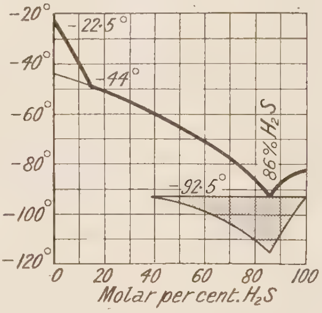

FIG. 39.—Freezing-point Curve of the System: CCl_4–H_2S.

	0°	5°	10°	15°	20°	24°
H_2S . .	17·891	14·776	11·992	9·539	7·415	5·955 vols.

or one vol. of alcohol absorbs $S=17·891-0·65598\theta+0·00661\theta^2$ vols. of hydrogen sulphide. W. H. McLauchlan also obtained values for the solubility of the gas in alcohol. G. Baume and F. L. Perrot measured the f.p. of mixtures of hydrogen sulphide and **methyl alcohol,** Fig. 36. There is a eutectic at $-132·9$°. A. M. Wasilieff made some observations on this subject. Hydrogen sulphide was found by W. Higgins to be soluble in **ether;** and G. Baume and F. L. Perrot measured the f.p. of mixtures of **methyl ether** and hydrogen sulphide, Fig. 36, and obtained eutectics at $-153·7$° and $-137·6$° with a maximum at $-148·6$° corresponding with $(CH_3)_2O.H_2S$. A. M. Wasilieff made some observations on this subject. For the solubility in vols. of hydrogen sulphide dissolved by one vol. of a soln. containing the following number of mols of **acetic acid,** CH_3COOH, in 100 mols of water at 25°, W. H. McLauchlan gave:

	0	8·85	21·0	53·5	67·8	98·58
H_2S . .	2·61	2·56	2·61	3·16	3·65	9·94 vols.

and for the solubility in one vol. of N-**tartaric acid,** he gave 2·46 vols. of gas, and in $3N$-$C_4H_3O_3$, 2·24 vols.; one vol. of a soln. of 60·1 grms. of urea per litre, dissolved 2·66 vols. of gas; and one vol. of a normal soln. of **ammonium acetate,** 2·84 vols. of gas. R. F. Marchand found that hydrogen sulphide is soluble in **methyl acetate.** A. W. Ralston and J. A. Wilkinson studied the thiohydrolysis of the **thioacetic ethers** in liquid hydrogen sulphide; and R. E. Meints and J. A. Wilkinson, the thiohydrolysis of **furfuraldehyde.** P. H. Lepage showed that **glycerol** dissolves less hydrogen sulphide than water; and W. H. McLauchlan found that one vol. of pure glycerol dissolves 2·26 vols. of the gas. Hydrogen sulphide is insoluble in **caoutchouc.** D. L. Hammick and W. E. Holt studied ternary systems of sulphur with quinoline, pyridine, and *p*-xylene. M. Berthelot[26] found that hydrogen sulphide completely displaces hydrogen cyanide from soln. of the **alkali cyanides,** and in dil. aq. soln., $(H_2S,2KCy)=4{\cdot}7$ Cals.: $(Na_2S,2HCy)=3{\cdot}2$ Cals.; $(Na_2S,HCy)=3{\cdot}1$ Cals.; $(NaHS,HCy)=0$ Cals.; and $(Na_2S,KCy)=0$ Cals. If hydrogen sulphide be added to a soln. of **silver cyanide** in an excess of potassium cyanide, a brown coloration is produced and subsequently a precipitate, but the filtrate contains a silver salt, hydrogen cyanide, and hydrogen sulphide. In the presence of a slight excess of potassium cyanide, the action of the hydrogen sulphide is complete; a considerable excess of the cyanide is necessary to keep the silver in soln. Sodium sulphide behaves like hydrogen sulphide. In the soln. there is a complex condition of equilibrium between hydrogen sulphide, hydrogen cyanide, and silver potassium cyanide, dependent on the relative stability of hydrogen silver cyanide and silver potassium cyanide, which is increased by the presence of excess of potassium cyanide, but reduced by an increase in temp. or the addition of acetic acid. The decomposition of silver potassium cyanide by hydrogen sulphide produces no thermal disturbance, and the occurrence of the reaction is determined by the removal of the silver sulphide from the sphere of action. In the presence of excess of potassium cyanide, which produces a development of heat over and above that corresponding with the formation of silver potassium cyanide, there is no precipitation. If the pure double cyanide is mixed with a quantity of hydrogen sulphide insufficient for complete precipitation, an intermediate condition is produced, and there is development of heat. The action of potassium cyanide soln. on freshly precipitated silver sulphide also causes considerable development of heat. The condition of equilibrium corresponds with the proportion $2AgK(CN)_2+K_2S+92KCN$, a double cyanide and sulphide being formed with development of heat. With mercuric potassium cyanide, the precipitation is complete; and with zinc potassium cyanide, the precipitation is slow, and if potassium cyanide is in sufficient excess there is no precipitation. E. Baumann studied the action of hydrogen sulphide on **aldehydes,** and **cyanic acid;** E. F. Smith and H. F. Keller, on the **metallamines;** and W. Schneider the action of the gas on **sugars**—dextrose furnishes thioderivatives; the hexoses—*d*-galactose, *d*-mannose, and *d*-fructose—act more rapidly than dextrose; the action with *l*-rhamnose and *l*-arabinose is similar; lactose and maltose react slowly; and α-methylglucoside and mannitol do not give thioderivatives. W. A. Plotnikoff obtained compounds with aluminium bromide and **ethyl bromide, ethylene bromide,** and **bromoform.** J. U. Nef studied the action of hydrogen sulphide on **silver fulminate;** and L. Cambi, on **mercury fulminate.** E. Schmidt showed that many of the **alkaloids**—*e.g.* strychnine, brucine, veratrine, nicotine, conine, cinchonine, etc.—react with hydrogen sulphide to form crystalline additive compounds.

U. Antony and G. Magri[27] reported that liquid hydrogen sulphide is a good **solvent** with small ionizing power, and D. McIntosh and co-workers observed that it dissolves metal salts sparingly; it dissolves hydrogen chloride and bromide without forming conducting soln.; but a number of organic compounds form conducting soln.—*e.g.* amines, acid amides, alkaloids, ketones, ether, methyl alcohol, phenols, organic acids, and ethers. Hydrogen sulphide is employed as a **reducing agent**—*e.g.* in converting ferric to ferrous salts, etc.—and L. Cohn[28] has discussed its use as a reducing agent in organic syntheses.

P. Sabatier[29] found that when **boron** is heated in hydrogen sulphide, boron sulphide is produced; while **silicon** furnishes silicon sulphide. The f.p. of the system **boron trifluoride** and hydrogen sulphide has two eutectics—one at −147·5°, and the other at 137·5°, Fig. 36. The maximum at −137° corresponds with **boron trifluodihydrosulphide,** $BF_3.H_2S$; and there is a transition point at −99° corresponding with **boron trifluotetradecahydroheptasulphide,** $BF_3.7H_2S$. M. Blix ound that only in the presence of aluminium chloride does boiling **silicon tetrabromide** react with hydrogen sulphide, forming silicon dibromosilicide. Many natural **silicates** were found by P. Didier to be attacked by hydrogen sulphide at 1400°. There is a change of colour, and the silicates become more soluble in acids, part of the metallic constituents having been converted into sulphides. The quantity which becomes soluble varies with the nature of the mineral from about 7 per cent. with peridote to 45 per cent. with powdered commercial cerite. In most cases a small quantity of sulphuric acid is formed, and condenses in the cool part of the tube. The silica displaced by the hydrogen sulphide remains in the free state, usually non-crystalline, or in some cases forms more acidic silicates. Occasionally an annular deposit forms in the cool part of the tube, consisting either of silicon or a silico-formic compound.

J. L. Gay Lussac and L. J. Thénard[30] found that when hydrogen sulphide is heated in the presence of **potassium** or **sodium,** the alkali hydrosulphide is formed: $2K+2H_2S=2KSH+H_2$; hence, 2 vols. of hydrogen sulphide furnish one vol. of hydrogen; with **tin,** stannous sulphide is formed and the hydrogen sulphide furnishes its own vol. of hydrogen. V. Merz and W. Weith found that the dried gas does not act on **copper** or **silver** unless air be present. If a mixture of air and hydrogen sulphide be passed over powdered copper, the mixture is sometimes heated to redness by the heat developed during the reaction: $4Cu+2H_2S+O_2=2H_2O+2Cu_2S$; with oxygen in place of air, the mixture is always heated to redness, and the cuprous sulphide is sintered together. J. B. Fournier and F. Lang observed no apparent alteration of copper after immersion for eleven years in liquid hydrogen sulphide at ordinary temp., or for 15 days at temp. up to 60°. According to M. Berthelot, the decomposition by copper begins at 500°, and by silver and **mercury** at 500°; mercury is not affected in the cold. According to M. Berthelot, when a mixture of hydrogen sulphide and oxygen is left in contact with mercury, the surface of the latter is slowly converted into sulphide, but the reaction does not continue unless the surface of the mercury is constantly renewed. The complete reaction would develop +74·8 Cals. H. St. C. Deville and L. Troost, and R. Lorenz studied the reaction with **silver;** and R. Lorenz, the action of the gas on **nickel, zinc,** and **cadmium;** and S. Meunier, on an **iron-chromium** alloy. G. Tammann and W. Köster studied the rate of attack of hydrogen sulphide on the metals. The action is rapid with copper and manganese; slower with silver; and slower still with lead. No change was observed with zinc, cadmium, tin, **aluminium, antimony, bismuth, chromium, iron, cobalt,** and nickel after several days' contact with the gas. J. B. Fournier and F. Lang found that aluminium and iron behaved like copper towards liquid hydrogen sulphide. The specific action of hydrogen sulphide is discussed in connection with the individual metals; a similar remark applies to the metal oxides, and the metal salts. The relative affinity of the metals for sulphur has been discussed in connection with elemental sulphur.[31] According to I. Guareschi, hydrogen sulphide is readily absorbed by **soda-lime,** which becomes black, possibly owing to the presence of impurities and the formation of iron sulphide. This reaction is attended with the development of a very considerable amount of heat, and when the current of gas is mixed with air the soda-lime becomes incandescent, whilst replacement of the air by oxygen results in a violent explosion. This incandescence is observed only with freshly prepared soda-lime, which should consist of granules 1 to 3 mm. in diameter. 100 grms. of soda-lime absorb as much as 35 litres of hydrogen sulphide. The incandescence observed when a mixture of air and hydrogen sulphide is passed over soda-lime also occurs when the latter is replaced by a mixture of lime or, more especially, **barium oxide** with sodium or potassium hydroxide, even when the latter is present in relatively small proportion; potassium hydroxide is more effective than sodium hydroxide. A negative result is obtained when the lime or baryta is replaced by **beryllium oxide.** The incandescence cannot be attributed to the presence or formation of peroxides; the **alkali peroxides** (not of recent preparation) act almost like hydroxides, and

barium, magnesium, and lead dioxides have no action. Mixtures of calcium or barium oxide with **mercuric oxide** or **nickel oxide** also react vigorously with hydrogen sulphide and, when the constituent oxides are in definite proportions, vivid incandescence or even explosion takes place. When incandescence occurs with mercuric oxide, sulphur dioxide is formed, and this reacts with the hydrogen sulphide, giving colloidal sulphur, which is precipitated by water in a special, blue form. No incandescence is observed when hydrogen sulphide acts on pumice and mercuric oxide, or on a mixture of calcium or barium oxide with **cuprous or cupric oxide, lead oxide,** or **ferric oxide.** H. B. Dunnicliff and S. D. Nijhawan found that when hydrogen sulphide is passed into a neutral soln. of **potassium permanganate,** the products are colloidal manganese dioxide, sulphur, and potassium sulphate and thiosulphate: $10KMnO_4+22H_2S=3K_2SO_4+2K_2S_2O_3+10MnS+22H_2O+5S$. The colloid afterwards coagulates. An excess of hydrogen sulphide furnishes manganese sulphide; and at the same time the dithionate passes into sulphate, and sulphur separates partly in a colloidal form. The property possessed by the **iron hydroxides** of removing hydrogen sulphide from coal-gas has been utilized for many years. The subject has been discussed by W. A. Dunkley and R. D. Leitch, and T. G. Pearson and P. L. Robinson—*vide* iron sulphide. H. B. Dunnicliff and C. L. Soni studied the action of hydrogen sulphide on **chromates**—*q.v.*—$2H_2CrO_4+3H_2S=2Cr(OH)_3+2H_2O+3S$.

G. N. Quam studied many reactions with liquid hydrogen sulphide as solvent. Salts with **hydrogen sulphide of crystallization,** or **sulphohydrate,** were prepared by W. Biltz and E. Keunecke[32]—*e.g.* $BeBr_2.2H_2S$; $BeI_2.2H_2S$; $AlCl_3.H_2S$; $AlBr_3.H_2S$ (studied by S. Jakubsohn); $AlI_3.2H_2S$; $AlI_3.4H_2S$; $TiCl_4.H_2S$; $TiCl_4.2H_2S$; $TiBr_4.H_2S$; $TiBr_4.2H_2S$; $SnCl_4.2H_2S$; and $SnCl_4.4H_2S$. E. Baud also prepared $AlCl_3.H_2S$, with aluminium chloride and liquid hydrogen sulphide at —70°; and at —45°, $2AlCl_3.H_2S$ appears. W. A. Plotnikoff prepared $AlBr_3.H_2S$. H. R. Chapman and D. McIntosh found that iodine, tri*iso*butylamine, tripropylamine, and antimony trichloride form conductive soln. with liquid hydrogen sulphide. R. W. Borgeson and J. A. Wilkinson, R. E. Meints and J. A. Wilkinson, and A. W. Ralston and J. A. Wilkinson studied reactions with organic compounds in the liquified gas.

According to R. E. Hughes,[33] hydrogen sulphide, when thoroughly dried, acts as an acid anhydride, since it does not react with many thoroughly dried metal oxides and salts. An aq. soln. of the gas acts as a weak dibasic acid—**hydrosulphuric acid**—forming a series of **sulphides** of the type R_2S, which may be regarded as normal sulphides. If only one of the hydrogen atoms is displaced by a metal, **hydrosulphides** of the type R.SH are formed. R. de Forcrand compared the chemical function of water, H_2O, with that of hydrogen sulphide, H_2S; in other words: Are the two compounds constituted alike? From the equations $H_2O_{soln.}+Na_{soln.}=H_{gas}+NaOH_{soln.}+31{\cdot}19$ Cals.; and $NaOH_{soln.}+Na_{soln.}=H_{gas}+Na_2O_{soln.}-11{\cdot}685$ Cals., it follows that the quantities of heat developed during the successive replacement by sodium of the hydrogen atoms in the water molecule differ by 42·875 Cals., which is an abnormally large difference. The corresponding heat changes for the action of sodium on hydrogen sulphide are 44·45 and 31·80 Cals., giving a difference of 12·65 Cals., and a mean value of 38·12 Cals. When the hydrogen atoms of the hydroxyl groups of catechol are successively replaced by sodium, the amounts of heat developed are 43·61 and 33·08 Cals. respectively, the difference being 38·42 Cals. From these numbers, R. de Forcrand concluded that hydrogen sulphide, considered thermally, is a true diphenol with the formula H—S—H, but that water is not a symmetrical compound and must be represented by the formula H—OH. J. Thomsen also concluded from his thermochemical observations that in a wet way only one hydrogen atom is replaceable by a metal, so that the constitution is H(SH), and that the acid in aq. soln. is monobasic, consequently, R(SH) represents a neutral salt. The sulphide K_2S is considered to be a molecular mixture of H(SK) and H(OK); and CaS, as a basic sulphide or oxysulphide, (HS)Ca(OH). H. Kolbe said that this hypothesis is supported by the fact that water decomposes normal barium sulphide, BaS, into the hydrosulphide and hydroxide; but not so with sodium sulphide, Na_2S. A soln. of sodium sulphide, $Na_2S.9H_2O$, when boiled with potassium ethyl sulphate, should yield mercaptan without any admixture of ethyl sulphide, if the action of water effected its complete decomposition into sodium hydrate and sodium hydrosulphide or sulphydrate. H. Kolbe found, however, that ethyl sulphide is the principal product of the reaction, being accompanied by more or less mercaptan, according to the conc. of the soln. employed; the more dil. the soln. the larger being the proportion of mercaptan. He therefore inferred that the metallic sulphides are only partially decomposed into hydroxides and hydrosulphides by soln., the extent of the decomposition depending on the proportion of water present. Observations on the electrical conductivity of the soln. also favour the hypothesis that hydrogen sulphide in aq. soln. is a dibasic acid whose two hydrogen can be displaced one by one, forming the respective ions HS′ and S″. K. Jellinek and J. Czerwinsky inferred from the great difference in the ionization constants and the heat of ionization of hydrogen sulphide that the molecule must possess an asymmetric structure. The sulphides and hydrosulphides are discussed in connection with the respective metals. E. Pietsch and co-workers studied the action of hydrogen sulphide on crystals of copper sulphate.

Some reactions of analytical interest.—Dil. **sulphuric acid** decomposes all soluble and some insoluble sulphides with the evolution of hydrogen sulphide; while the conc. acid decomposes all the sulphides when warmed, forming sulphur and sulphur dioxide: $Na_2S+2H_2SO_4=Na_2SO_4+2H_2O+SO_2+S$; the sulphur itself may also form sulphur dioxide under these conditions: $S+2H_2SO_4=2H_2O+3SO_2$. A black precipitate of silver sulphide is produced by **silver nitrate**; the precipitate is insoluble in cold nitric acid, but soluble in the warm acid; **lead salts** give a black precipitate of lead sulphide; paper saturated with a soln. of lead acetate is a common form of applying the test for the gas. A soln. of **barium chloride** gives no precipitate. According to E. Tiede and F. Fischer,[34] if a soln. of **mercuric chloride** be added drop by drop to a conc. hydrochloric acid soln. containing a little hydrogen sulphide, a lemon-yellow turbidity or precipitate is formed. The reaction is said to be very sensitive. A reddish-violet colour is produced when a soluble sulphide—not hydrosulphide—is treated with **sodium nitroprusside.** Hence a soln. of hydrogen sulphide does not give the reaction except when treated with alkali-lye. A number of other tests based on the reducing action of the gas could be devised. Thus, according to D. Ganassini, a soln. of 1·25 grms. of **ammonium molybdate** in 50 c.c. of water is mixed with a soln. of 2·5 grms. of potassium thiocyanate in 45 c.c. of water, and to the mixture are added 5 c.c. of hydrochloric acid. The reagent will keep for a few days when placed in the dark. A strip of filter-paper or a porcelain slab moistened with the reagent when exposed to vapours containing hydrogen sulphide will turn red. In the so-called **methylene-blue test** of N. Caro and E. Fischer, the aq. soln. of hydrogen sulphide is treated with one-fiftieth vol. of conc. hydrochloric acid, a few grains of paramidodimethylaniline sulphate are added, and when this is dissolved, 1 to 2 drops of a dil. soln. of ferric chloride. In the case of a soln. containing 0·00009 grm. hydrogen sulphide in a litre of water, coloration took place in a few minutes, and in half an hour the liquid had assumed a strong blue colour, which lasted for days. A soln. of the same conc., but without hydrochloric acid, yielded only a light brown coloration with lead acetate. In a soln. containing 0·0000182 grm. of hydrogen sulphide in a litre of water, the methylene-blue reaction still gave a distinct blue coloration, whilst no effect was produced either by lead acetate or sodium nitroprusside. This reaction is therefore recommended as the most delicate and certain test for neutral or acid soln. of hydrogen sulphide. Numerous **oxidizing agents**—the halogens, nitric acid, chromates, permanganates, ferric salts, etc.—decompose hydrogen sulphide with the separation of sulphur. **Silver** is blackened by free hydrogen sulphide, or by soluble sulphides. The blackening occurs only if air or oxygen be present : $2Ag+H_2S+O(air)=H_2O+Ag_2S$; or $2Ag+Na_2S+H_2O+O(air)=2NaOH+Ag_2S$.

Hydrogen sulphide is a valuable reagent. In 1831, J. von Liebig,[35] in a *Note sur la séparation de quelques oxides métalliques dans l'analyse chimique*, showed that its reactions with the different metal salts enable the metals to be separated into groups as a preliminary to more detailed examination. Thus—

I. Sulphides insoluble in dil. acids.

(*a*) Soluble in alkaline sulphides—arsenic, antimony, stannic, gold, germanium, molybdenum, tellurium, tungsten, iridium, and platinum sulphides.

(*b*) Insoluble in alkaline sulphides—mercury, silver, lead, copper, bismuth, cadmium, and stannous sulphides.

II. Sulphides soluble in dilute mineral acids but insoluble in the presence of alkalies—iron, cobalt, nickel, manganese, and zinc sulphides.

III. Sulphides not precipitated by hydrogen sulphide—chromium, aluminium, magnesium, barium, strontium, calcium, potassium, and sodium. Chromium and aluminium are precipitated as hydroxides.

An alternative scheme for the grouping of the elements for the purpose of analysis is based on the behaviour of solutions of their salts towards ammonium sulphide.

1. Sulphides soluble in ammonium sulphide—arsenic, antimony, and tin.
2. Sulphides or hydroxides precipitated by ammonia and ammonium sulphide.

(*a*) Insoluble in cold dilute hydrochloric acid—mercury, lead, bismuth, cadmium, copper, nickel, and cobalt.

(*b*) Soluble in cold dilute hydrochloric acid—zinc, maganese, iron, aluminium, and chromium.

Silver, lead, and mercury can be first precipitated by hydrochloric acid, and barium, strontium, calcium, and lead by sulphuric acid. Other modifications can be introduced.

The method of classifying certain elements into groups—those which form soluble and those which form insoluble sulphides in hydrochloric acid—frequently conveys wrong ideas of the properties of the sulphides. The solubility of the sulphides depends upon the conc. of the acid. For instance, if hydrogen sulphide be passed into 5 c.c. of a soln. of 2 grms. of tartar emetic—potassium antimonyl tartrate—in 5 c.c. of hydrochloric acid (sp. gr. 1·175) and 85 c.c. of water, antimony sulphide will be precipitated, but not if 15 c.c. of hydrochloric acid had been employed without the water. In one case, $2SbCl_3+3H_2S=Sb_2S_3+6HCl$; and in the second case, $Sb_2S_3+6HCl=3H_2S+2SbCl_3$. In other words, the antimony sulphide, in the second case, is decomposed by the acid as fast as it is formed. Similarly, no lead will be precipitated by hydrogen sulphide from a soln. containing 3 per cent. of hydrochloric acid, HCl ; and if the soln. has 2·5 per cent. of acid, the lead sulphide will be imperfectly precipitated—*i.e.* part will be precipitated, and part will be decomposed as fast as it is formed. Similarly, a 5 per cent. boiling soln. of hydrochloric acid will prevent the precipitation of cadmium sulphide.

If a metallic sulphide, MS, be treated with hydrochloric acid, hydrogen sulphide and a metallic chloride will be formed: $MS+2HCl=MCl_2+H_2S$. Conversely, when a metallic chloride in aq. soln. is treated with hydrogen sulphide, the metallic sulphide and hydrochloric acid will be produced : $MCl_2+H_2S=MS+2HCl$. Hydrochloric acid thus accumulates in the soln. as the action goes on. If any more sulphide be produced, after the hydrochloric acid has attained a certain limiting concentration, the excess of sulphide will be at once decomposed by the acid. There are then two simultaneous opposing reactions : (1) Formation of the metallic sulphide and hydrochloric acid ; and (2) formation of chloride and hydrogen sulphide. In illustration, if a current of hydrogen sulphide be passed through a sat. soln. of zinc chloride, part of the metal is precipitated, but when the hydrochloric acid has attained a certain concentration, the action apparently ceases because the reverse change sets in. Hence, the precipitation will be incomplete. In illustration, take the case of lead chloride : $PbCl_2+H_2S\rightleftharpoons PbS+2HCl$. When equilibrium is established, the soln. contains lead chloride, hydrogen sulphide, and hydrogen chloride. Using symbols in square brackets to represent the conc. (g. mol. per litre) of the respective compounds in the soln., it follows from the equilibrium law, that: $[PbCl_2]\times[H_2S]=K[HCl]^2$. This shows that if the conc. of the acid be increased, and the conc. of the hydrogen sulphide be constant, the amount of lead chloride which remains in soln. (that is, escapes precipitation) will increase in order to keep the numerical value of the "constant" always the same. Conversely, if it be desired to keep the amount of lead chloride in the soln. as low as possible, it is necessary to keep the conc. of the acid down to a minimum value. A certain amount of acid is usually required to keep other metals in soln.; zinc, for example. See the individual metals.

The conc. of the hydrogen sulphide in the soln. is practically constant (0·0073 mol. per litre at 20°) when the gas is passing through the soln. If the conc. of the hydrogen sulphide were large and the conc. of the metallic chloride small, a very large excess of acid would be needed to prevent metal being precipitated by the hydrogen sulphide. It will be observed, however, that the conc. of the hydrogen sulphide under ordinary circumstances is small. In consequence, a comparatively small amount of acid suffices to prevent the separation of sulphides of zinc, iron, nickel, cobalt, and manganese. If the solubility of the hydrogen sulphide has been greater than it is, some of the metals—zinc, iron, nickel . . .—would have been included in the "hydrogen sulphide group"; and conversely, had the solubility of hydrogen sulphide been less than it is, some of the present members of the "hydrogen sulphide group" would not have been there. For instance, tin, lead, cadmium. . . . Molybdenum is precipitated incompletely under ordinary press., but if the soln. be warm and the press. of the gas be increased, it can be completely precipitated. This subject was discussed by G. Bruni and M. Padoa.

Under ordinary conditions, the solubilities of the sulphides in hydrochloric acid, starting with the least soluble, are approximately in the order: Mo, Pt, Au, As, Ag, Cu, Sb, Bi, Sn(ic), Hg, Cd, Pb, Sn(ous), Zn, Ti, Fe, Ni, Co, Mn. As shown by G. Bodländer, W. Böttger, and O. Weigel, the conditions of precipitation affect the results to some extent. G. Bodländer gave for the solubilities in mols $10^6\times$ per litre, MnS, 71·6; ZnS, 70·1; FeS, 70·1; CoS, 41·62; NiS, 39·87; CdS, 8·836; ZnS, 6·63; Sb_2S_3, 5·2; PbS, 3·60; CuS, 3·51; Cu_2S, 3·10; As_2S_3, 2·1; SnS_2, 1·13; Ag_2S, 0·552; Bi_2S_3, 0·35; SnS, 0·14; and Hg_2S, 0·054. Elements wide apart in the list can be easily separated by hydrogen sulphide in acid soln., but elements close together in the list require a very careful adjustment of the amount of acid in soln. before satisfactory separations can be made. For instance, the separation of cadmium or lead from zinc by means of hydrogen sulphide is only satisfactory when the conc. of the acid is very carefully adjusted. If too much acid be present, cadmium or lead will be imperfectly precipitated; while if too little acid be present, zinc will be precipitated with the cadmium or lead. Hence there is no sharp line of demarcation between metals precipitated and metals not precipitated by hydrogen sulphide from acid soln. All depends upon the conc. of the acid. This is arbitrarily adjusted so that antimony, arsenic, lead, bismuth, cadmium, copper, mercury, and tin are precipitated by making the vol. of the soln. such that it contains approximately 4 c.c. of hydrochloric acid (sp. gr. 1·12) per 100 c.c. before passing the hydrogen sulphide. The aluminium, iron, zinc, nickel, cobalt, and manganese salts will be found in the filtrate. Barium, strontium, calcium, and magnesium salts will also be found in the filtrate along with alkalies, because the sulphides of these elements are attacked and decomposed by water and by acids. *E.g.* $2CaS+2H_2O \rightleftharpoons Ca(OH)_2+Ca(SH)_2$.

The above remarks can be easily translated into the language of ions. The precipitation is then supposed to proceed according to the equation: $M^{\cdot\cdot}+2H_2S \rightleftharpoons M(HS)_2+2H^{\cdot}$; or $M^{\cdot\cdot}+H_2S \rightleftharpoons MS+2H^{\cdot}$. That is, the bivalent ion $M^{\cdot\cdot}$ reacts with the hydrogen sulphide, forming the sparingly soluble MS, or $M(HS)_2$, which precipitates. In the process, hydrogen (acid) ions, $H^{\cdot}$, are formed.

The hydrogen sulphide is itself supposed to be ionized in aq. soln. as indicated above: $H_2S \rightleftharpoons H^{\cdot}+HS \rightleftharpoons 2H^{\cdot}+S''$. The metal chloride, say, is also ionized: $MCl_2=M^{\cdot\cdot}+2Cl'$. Hence the soln. may be supposed to contain $MCl_2+H_2S \rightleftharpoons M^{\cdot\cdot}+2Cl''+S''+2H^{\cdot}$. When the solubility product $[M^{\cdot\cdot}]\times[S'']$ is exceeded, the solid MS separates from the soln., leaving hydrochloric acid ions behind: $2H^{\cdot}+2Cl'$. A further amplification on the lines indicated in the text can now be made. Here, as elsewhere, it makes very little difference which mode of expression be used. The facts will stand for ever; the language used in describing the facts, like other customs, changes according to the prevailing fashions.

The physiological action of hydrogen sulphide.—The aq. soln. and the gas are poisonous, but less poisonous than chlorine or bromine. Towards the end of the eighteenth century, a number of accidental deaths occurred in Paris, due to the gases from the sewers; and in 1785, M. Hallé [36] reported on the conditions, but did not recognize hydrogen sulphide as the cause of the poisoning. At the beginning of the nineteenth century, G. Dupuytren, M. Prunelle, and F. Chaussier proved that hydrogen sulphide was present in the mephatic vapours from the sewers, and it was believed that this gas was the cause of the toxic action of the sewer gas. M. Parent-Duchatelet made a comprehensive report on the Paris sewers in 1829; he found that the average proportion of hydrogen sulphide was 2·29 per cent. Cases of accidental poisoning were reported by T. S. Bell, B. I. Raphael, L. Holden and H. Letheby, R. Christison, H. Letheby, A. Kwilecki, D. Brown, R. R. Sayers and co-workers, A. Haibe, K. B. Lehmann, A. Cahn, J. P. J. d'Arcet and H. Braconnot, etc. Observations on sewer-gas poisoning were also made by T. H. Barker, and L. Surne. C. W. Mitchell and S. J. Davenport say that hydrogen sulphide is one of the most toxic gases, and is comparable to hydrogen cyanide with respect to rapidity of action and concentration producing death. The action depends upon the concentration—0·005 per cent. is sufficient to produce poisoning, while a continued exposure to a conc. of 0·02 per cent. during several days may produce death. The exact mechanism of the poisoning is unknown. A. S. Taylor described the cases of hydrogen sulphide poisoning which occurred during the building of the tunnel under the Thames. T. Oliver mentioned three fatal cases in the construction of a graving dock at Hebburn-on-Tyne, where the excavation reached some old alkali waste; and A. S. Taylor mentioned six fatal cases at Cleator Moor. Some cottages were built on iron slag; the slag contained sulphides of calcium and iron; the water from a heavy rainstorm soaked into the slag, and hydrogen sulphide was formed; this diffused into the cottages during the night, and killed three adults and three children. Hydrogen sulphide is a common reagent in chemical laboratories. A. Cahn described the case of a student poisoned by the gas in the laboratory. J. Habermann and co-workers examined fifty samples of air from laboratories, and found the hydrogen sulphide varied from 0·00015 to 0·2 vol. per 1000. R. Biefel and T. Polek, and A. Haibe described cases of hydrogen sulphide poisoning in the coal-gas industry; T. Oliver, in the sulphur mines of Sicily; and M. Holtzmann, in tanneries. According to C. B. Lehmann, an atmosphere containing 1 : 3000 hydrogen sulphide kills cats and rabbits in 10 minutes; an atmosphere with 0·4 to 0·8 per 1000 produces local irritation on the mucous membrane of the respiratory tract, and death follows from an œdema of the lung preceded by convulsions; air containing 0·2 per 1000 produces in half an hour a smarting of the eyes, nose, and throat, and after 30 minutes the atmosphere can no longer be borne, air with 0·5 per 1000 is the utmost that can be breathed, and it produces smarting of the eyes, nasal catarrh, cough, palpitation, shivering, great muscular weakness, headache, and faintness with cold sweats. 0·76–0·8 per 1000 is dangerous to human life, and 1·0–1·5 per 1000 rapidly destroys life. H. W. Haggard and Y. Henderson studied the action of hydrogen sulphide on the respiratory centres. R. Fisher compared the toxic action of the gas alone, and when associated with carbon disulphide. E. Goldsmith found that three men exposed to the gas became temporarily blind for 2 or 3 days, suffering with intense pain, with reddening of the conjunctiva; almost continual running of tears; headache and general indisposition. He supposed that the gas formed a compound in the outer cuticle of the eye, and that this prevented light passing into the eyes. The patients could not distinguish objects held before them; they could not find their way home alone. The eyesight always returned after the lapse of several days. J. Wigglesworth reported two cases of insanity produced by the inhalation of hydrogen sulphide. H. Schulz said that the gas acts as a hypnotic agent, but N. Uschinsky could find no evidence of this. Observations on hydrogen sulphide poisoning were also made by C. Bernard, H. Eulenberg, R. Biefel and T. Polek, W. Kühne, P. Brouardel and P. Loye, A. Flint, E. Salkowsky, H. Stifft, and C. Husson.

J. R. Wilson observed that 1 per cent. of hydrogen sulphide in the air kills a rabbit in about a minute; 0·5 per cent., in 3 minutes; 0·2 per cent., in 10 minutes; 0·1 per cent., in 37 minutes; and 0·025 per cent. produced no perceptible result on a rabbit after 2 hrs.' inhalation. The toxic effect on bacteria was observed by F. Hatton, and C. Fermi. A. Chauveau and J. Tissot found that animals live quite well in a lethal atmosphere of hydrogen sulphide provided that they are allowed to breathe pure air through a tube. Hence, the skin and external mucous membranes are impermeable. This contradicts an early observation by F. Chaussier. J. P. Peyron, and L. Simirnoff examined the absorption of hydrogen sulphide by contact with different parts of animals.

The gas is a blood poison. F. Hoppe-Seyler studied the chemical action of hydrogen sulphide on the blood. He observed that when hydrogen sulphide is passed through the blood, a dark green pigment is deposited similar to the greenish discoloration of cadavers. This change is said to be due to the action of hydrogen sulphide on the oxyhæmoglobin of the blood, with the formation of a substance termed *sulphmetahæmoglobin.* An absorption spectrum was found with two bands in the red—one near the *C*-line, and the other between the *C*-line and *D*-line. Observations were also made by T. Arake, A. Lewisson, A. Gamgee, W. Kühne, J. V. Laborde, E. Harnack, T. W. Clarke and W. H. Hurtley, A. van der Beigh, S. West and W. Clarke, R. L. M. Wallis, and P. Binet. N. Uschinsky said that the poisonous action is not due to the formation of a sulphometahæmoglobin, and O. Pohl attributed it to the gas uniting with the alkali of the blood, forming alkali sulphides, but H. W. Haggard disproved this hypothesis. S. Kaufmann and I. Rosenthal attributed the action of hydrogen sulphide to be such as to result in oxygen-hunger, and compared hydrogen sulphide poisoning with suffocation; but F. Hoppe-Seyler showed that this explanation is incomplete, because it does not explain the action of the gas on the nervous system.

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§ 10. The Polysulphides of Hydrogen

In 1777, C. W. Scheele,[1] during his work on the phlogistification of sulphur, discovered a polysulphide of hydrogen. He said:

> If you pour into a solution of sulphur in alkali a great deal of acid at once, a small quantity of *stinken de Luft*—*i.e.* hydrogen sulphide—is evolved, and you may observe in this mixture a kind of thin oil; however, the oil remains not fluid always, but grows thick and hard in the open air. It seems that the excess of acid immediately seizes upon the alkali; and since in that case no decomposition, or at least a very partial one, of the sulphur is possible, the heat obtains too small a quantity of phlogiston to expand the heavy sulphur into an airy vapour; a beginning only being made by forming an oil.

C. L. Berthollet then examined the oily liquid obtained by the action of acids on the polysulphides of the alkalies and alkaline earths, and concluded that its composition is H_2S_5. J. J. Berzelius regarded it as at least a pentasulphide or a still higher proportion of sulphur. L. J. Thénard obtained it both as a light, ethereal oil, and as a heavy, viscid oil. The difference was attributed to the latter containing a higher proportion of sulphur. He considered, by analogy with hydrogen peroxide which he discovered in 1818, that the light, ethereal oil had a similar composition, and he regarded it as **hydrogen persulphide,** H_2S_2. The oily liquid thus came to be called hydrogen persulphide, although a score of names had been previously applied to the oil. L. J. Thénard's analyses of the heavy oil varied from H_2S_7 to H_2S_9. A. W. Hofmann prepared a complex salt with strychnine, $C_{21}H_{22}N_2O_2.H_2S_3$, but later, he showed that the composition was better represented by the formula $(C_{21}H_{22}O_2N_2)_2.H_2S_6$. Compounds of H_2S_6 with brucine, $(C_{23}H_{26}O_4N_2)_2.H_2S_6$, and with benzylamine $(C_7H_7N)_2.H_2S_6$, were also prepared by E. Schmidt, and G. Bruni and A. Borgo. O. Döbner also prepared a compound with brucine, $(C_{23}H_{26}O_4N_2)_2.H_2S_8.2H_2O$. H. Brunner and V. Vuillellmier obtained complexes with benzaldehyde, $(C_6H_5COH)H_2S_3$; with anisic aldehyde, $(C_6H_4O.CH_3COH)H_2S_4$; with cinnamic aldehyde, $(C_9H_8O)H_2S_4$; and with benzoquinone, $(C_6H_4O_2)_4H_2S_5$.

W. Ramsay's analyses ranged from H_2S_7 to H_2S_{10}. P. Sabatier obtained from calcium polysulphide and hydrochloric acid an oil with a composition ranging between H_2S_6 and H_2S_{10}; and when the oil was distilled in vacuo, the product had the composition H_4S_4. H. Rebs obtained from sodium di-, tri-, tetra-, and penta-sulphide, as well as from the polysulphides of potassium and barium, by treatment with well-cooled hydrochloric acid, an oil which in all cases had the composition H_2S_5. This statement was not confirmed by I. Bloch and F. Höhn. The attempt by G. Bruni and A. Borgo to determine the mol. wt. from the effect of the persulphide on the f.p. of bromoform was shown by E. Paterno to be unreliable. The properties of the persulphide were examined by J. von Liebig, G. Kemp, R. Bunsen, C. F. Schönbein, P. Sabatier, and E. Drechsel.

Hydrogen persulphide is made by pouring a soln. of the polysulphide into hydrochloric acid; if this operation be reversed, no persulphide is formed, but the salt is decomposed: $CaS_5+2HCl-CaCl_2+H_2S+4S$. M. Berthelot said that it is best to employ an alkali polysulphide prepared by saturating a soln. of the normal sulphide with hydrogen sulphide with the air excluded so as to avoid the formation of thiosulphate which is decomposed by the acid with sulphur, etc. O. von Deines obtained hydrogen persulphide by reducing sulphur dioxide—gaseous or in aq. soln.—with hypophosphorous acid and extracting the product with ether. The sulphur dissolves in the hydrogen persulphide. O. von Deines explained the production of hydrogen persulphide by the action of $3N$-HCl on a soln. of sodium thiosulphate by assuming that sulphoxylic acid is formed as an intermediate product: $H_2S_2O_3=SO+H_2SO_2$, and that this reduces the sulphur dioxide which is also formed: $H_2S_2O_3=SO_2+H_2S+O$. Precipitated white sulphur is said to contain some hydrogen persulphide. The preparation of the polysulphide, and of hydrogen persulphide was described by J. J. Berzelius, L. J. Thénard, F. Höhn, I. Bloch and F. Höhn, etc. A. W. Hofmann, and E. Schmidt mixed ammonium polysulphide with a cold, saturated soln. of strychnine in alcohol; and treated the crystalline product with conc. sulphuric acid. The composition of the oil corresponded with H_2S_3.

What is here called hydrogen persulphide is doubtless a mixture. Hydrogen persulphide is a yellow, oily liquid, which, according to L. J. Thénard, is mobile if it contains a small proportion of sulphur, and viscid if it contains a large proportion. It has a peculiar, sulphurous, disagreeable odour, and irritates the eyes and nose; it tastes sweet and bitter; and imparts a white colour to the tongue and saliva. A few drops placed on the skin of the arm, alter and decolorize it. At the moment of its formation, the liquid bleaches litmus. C. F. Schönbein also found that it bleaches litmus and indigo. The colour is restored by oxidizing agents—ozone, chlorine, bromine, iodine, potassium permanganate, ozonides, hydrogen dioxide, etc.—by metallic salts—copper, manganese, nickel, and ferrous sulphates—and by phosphoric and arsenic acids; nitric and sulphuric acids act very slightly in the same way, and hydrochloric acid does not act at all. L. J. Thénard gave 1·769 for the sp. gr., and H. Rebs, 1·71 at 15°. P. Sabatier said that it can be distilled between 60° and 85° at a press. of 40 to 100 mm. A brilliant, pale yellow, limpid liquid distillate is produced which has a very irritating odour. The composition approaches H_2S_5. The heat of formation is $H_2S_{gas}+(n-1)S_{gas}=H_2S_n-5{\cdot}3$ Cals.; or $H_2+nS_{solid}=H_2S_n-0{\cdot}7$ Cal., when $n=6$ to 10. E. Becquerel gave 1·8850 for the index of refraction; and 1·743 for the magnetic rotation of the plane of polarized light.

L. J. Thénard said that when hydrogen persulphide is ignited by the flame of a candle, it burns with a blue flame. When the oxide of gold or silver is placed in contact with the liquid persulphide, it becomes red-hot, and the oxide is reduced to metal; but J. von Liebig said that silver oxide is converted into sulphide. According to L. J. Thénard, if the acid be left to itself for a few days, it is resolved into hydrogen sulphide and sulphur, so that the liquid becomes more and more viscid, and ultimately solid. The decomposition is rapid at 60°, and still more so at 100°.

P. Sabatier found that stability of the persulphide is increased by the presence of dissolved sulphur or hydrogen sulphide. Its decomposition is accelerated by light. Certain substances have no appreciable action on it. Amongst these are dry air, dry hydrogen, and conc. acids. Others, including carbon bisulphide, benzene and similar hydrocarbons, paraffins, and chloroform, simply dissolve it; whilst others, such as iodine, bromine, and potassium permanganate, act on the sulphur or hydrogen sulphide dissolved by the persulphide, and thus diminish its stability. Many substances which decompose the persulphide, such as alkalies, water, alcohols, and ethers, appear to form with it highly unstable intermediate compounds. L. J. Thénard found that the decomposition of the persulphide is more rapid at 100° than it is at 60°; while G. Kemp, and J. von Liebig showed that even when sealed up in a glass tube for 3 weeks, it forms transparent sulphur, and colourless liquid hydrogen sulphide. R. Bunsen said that the decomposition in a sealed tube occurs only when moisture is present; and if a little calcium chloride be present the liquid may be preserved without decomposition; but with finely divided calcium chloride, J. von Liebig said that hydrogen persulphide froths up violently and soon solidifies; effloresced sodium sulphate acts more slowly, but the crystals of the hydrate do not act at all. J. J. Berzelius showed that acids hinder or prevent the decomposition, while the decomposition was shown by L. J. Thénard, and J. von Liebig to be accelerated by finely-divided charcoal, silica, pyrolusite, kermes-mineral, galena, gold sulphide, gold, platinum, and other metals; but sugar, starch, and lignine exert a feeble action in hastening the decomposition. Potassium pentasulphide either in soln. or diffused in water causes a very violent evolution of hydrogen sulphide, and a sudden precipitation of sulphur; and an alcoholic soln. of liver of sulphur decomposes the persulphide without the evolution of gas. According to J. J. Berzelius, and L. J. Thénard, the decomposition of the persulphide is favoured by powdered hydroxides of potassium, the alkaline earths, and magnesia, and also by an aq. soln. of ammonia or potassium hydroxide. It is possible that these substances act by first forming sulphides. With a small proportion of potash-lye, hydrogen persulphide gives off hydrogen sulphide, and with an excess of alkali it at once forms spongy sulphur. P. Sabatier said that the rapid decomposition by alkalies is probably due to the formation of an unstable intermediate alkali sulphide. E. Drechsel represented the reaction with an alcoholic soln. of potassium sulphide: $2KSH+H_2S_5=K_2S_5+2H_2S$. According to L. J. Thénard, water removes hydrogen sulphide from the persulphide and becomes turbid; alcohol acts similarly, while ether dissolves it at first, but soon deposits acicular crystals of sulphur. E. Drechsel said that the persulphide is insoluble in water, alcohol, ether, benzene, and chloroform; and is decomposed by nitrobenzene and aniline. P. Sabatier said that a mixture of ether and hydrogen persulphide deposits nacreous sulphur in a short time; ethyl acetate, and ethyl or amyl alcohol act slowly; and hydrocarbons, and derivatives of chloroform do not give this reaction. For the observations of E. Schmidt, G. Bruni and A. Borgo, and H. Brunner and V. Vuillellmier, on the complex salts with hydrogen sulphide, *vide supra*. F. Höhn, and I. Bloch and co-workers observed that aldehydes react with the persulphide—*e.g.* benzaldehyde, and salicylaldehyde—forming thiocarbonic acids; I. Bloch and M. Bergmann found that with aromatic acid chlorides, acyl disulphides are formed. J. Dodnoff and H. Medox found that dimethylaniline causes a vigorous decomposition of hydrogen disulphide into hydrogen sulphide and sulphur. Triethylphosphine and triethylarsine afford the corresponding sulphides. With phosphorus trichloride in benzene the disulphide yields phosphoryl thiochloride, phosphorus pentasulphide, hydrogen chloride, and a little hydrogen sulphide. It appears probable that the compound $PCl_3(SH)_2$ is formed initially and that a similarity in constitution exists between hydrogen disulphide and hydrogen dioxide.

The nature of the lower hydrogen persulphides was worked out by I. Bloch and co-workers, and described in their papers: *Ueber Wasserstoffpersulfid*, in 1908. By heating sodium sulphide with varying amounts of sulphur in an atmosphere of hydrogen for three hours on the water-bath and dissolving the products in water, solutes of the composition Na_2S_2, Na_2S_3, Na_2S_4, and Na_2S_5, are produced. When the soln. are allowed to flow into mixtures of equal parts of ice and hydrochloric acid (D 1·19) cooled in a freezing mixture, crude hydrogen persulphide is obtained as a yellow, oily liquid with the odour of sulphur chloride and camphor. It is decomposed instantaneously by alkalies, and therefore it is essential that all apparatus used in the preparation should be washed with an acid. The oil can be kept for an hour without visible decomposition. Water decomposes it, but dil. acids, particularly hydrochloric acid, act as preservatives. A criterion of purity is the fact that the freshly prepared persulphide yields a clear soln. in benzene. Alcohols, ether, ethyl acetate, and acetone decomposes the oil more or less rapidly, whilst with aldehydes and ketones condensation occurs, yielding substances rich in sulphur. The crude oil is then to be fractionally distilled under reduced press., say, 20-25 mm. The distillation is conducted in an apparatus, Fig. 40, in which large quantities can be operated upon in small portions at a time, and the residue from an operation can be recovered after each distillation without disconnecting the apparatus. By using quartz vessels wherever possible, J. H. Walton and L. B. Parsons increased the yields, by lessening the tendency for the polysulphide to decompose. The flask *A*, of 300 c.c. capacity, immersed in the glycerol bath *K*, is connected through the condenser with *B* (150 c.c.), which is attached to the strongly-cooled vessel *C*—say by solid carbon dioxide and ether. By means of a tube reaching to the bottom, *A* is connected with the U-tube *F*. Between *H* and the water-pump are vessels containing soda-lime and calcium chloride, and a manometer. The flask *A* can be connected with the pump either through *B* and *C* by means of the stopcock *a*, or through *F* by the stopcock *b*. To prevent the deposition of sulphur during the distillation, dry hydrogen chloride should be passed through the apparatus before it is evacuated. To carry out the distillation, the bath *K* is raised to 110°–125°, and the apparatus evacuated to about 20 mm., *a* being open and *b* closed. From the dropping funnel *D*, about 15 c.c. of crude hydrogen persulphide is run slowly into *A*. Distillation commences; when it becomes irregular, *a* is closed and *b* opened, whereby the residue in *A* is drawn over into *F*. The distillation is then continued by closing *b*, opening *a*, and introducing another 15 c.c. of hydrogen persulphide into *A* from *D*. The liquid collecting in *B* is mainly hydrogen trisulphide, whilst the more volatile disulphide is found in *C*.

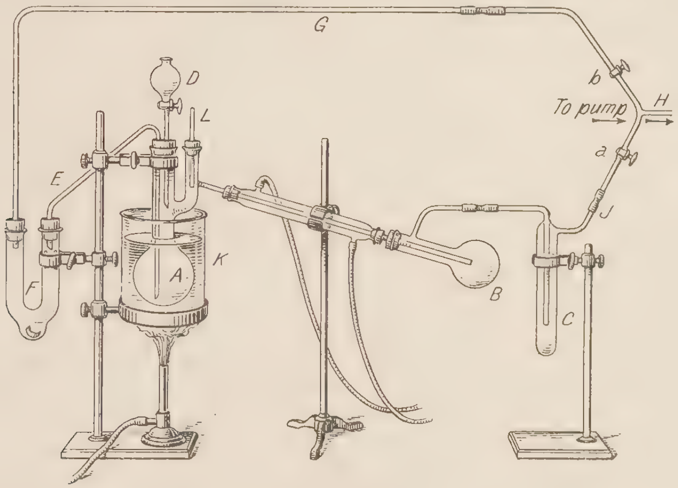


FIG. 40.—The Preparation of Hydrogen Di- and Tri-sulphides.

The crude hydrogen persulphide is separated into three fractions; the more volatile one collecting in *C*, Fig. 40, contains **hydrogen disulphide,** H_2S_2. It forms an almost colourless liquid as mobile as water. Its odour is more penetrating and aggressive than that of the trisulphide. The disulphide can be distilled with partial decomposition, at ordinary press., the chief fraction passes over at 74°–75°. The sp. gr. is 1·376 at 15°. The disulphide does not freeze in a mixture of solid carbon dioxide and ether, and J. H. Walton and L. B. Parsons found that it shows no sharp solidification temp. when cooled, but its m.p. is between $-88°$ and $-90°$; and its b.p. is 74·5°. I. Bloch and F. Höhn gave 74°–75° for the b.p., and added that the disulphide resembles the trisulphide in many respects, but it is more sensitive to soln. of the alkalies.

The oil which collects in receiver *B* during the distillation of crude hydrogen persulphide is **hydrogen trisulphide,** H_2S_3, a yellow oily liquid rather more mobile than olive oil. R. Schenck and V. Falcke found that the analyses and mol. wt. agree with H_2S_3. According to I. Bloch and F. Höhn, hydrogen trisulphide has a disagreeable odour, recalling that of sulphur monochloride and camphor. The vapour irritates the eyes and mucous membranes of the nose *sehr stark*. As in the case of ordinary sulphur, the yellow colour disappears when the trisulphide is cooled. Its sp. gr. is 1·496 at 15°. It freezes between $-53°$ and $-54°$ to a crystalline solid which melts to a colourless liquid between $-52°$ and $-53°$. This temp. was confirmed by J. H. Walton and L. B. Parsons. On cooling to $-78°$, the trisulphide became more and more viscous, like glass until it solidified. Attempts to distil the trisulphide at ordinary temp. were not successful; but when distilled under reduced press., 100 c.c. of the trisulphide furnished about 15 c.c. of disulphide, and 10 c.c. of residue; the remainder was collected as trisulphide. R. Schenck and V. Falcke gave 43°–50° for the b.p. at 4·5 mm. press. I. Bloch and F. Höhn found that when the trisulphide is warmed in a test-tube it darkens in colour, and becomes more and more viscid, and at about 90° there is a copious evolution of hydrogen sulphide; some drops of a distillate collect in the upper part of the tube. When the trisulphide has stood for about a day in darkness, it seems to have undergone no change, but after standing a longer time it decomposes with the separation of rhombic sulphur. It decomposes more quickly in light. When the liquid is shaken in a test-tube, bubbles of hydrogen sulphide are set free, and rhombic sulphur is precipitated. J. H. Walton and L. B. Parsons observed that when the trisulphide is kept in a sealed tube under ordinary laboratory conditions, at the end of 3 days small crystals of sulphur began to appear, while at the end of 5 days there were two liquid layers noticeable, the one heavy and viscous, the other light, mobile, and colourless, presumably hydrogen sulphide. There were large crystals of sulphur in the tube. After 2 days more, the viscous layer had completely disappeared, and the tube contained only several large rhombic crystals of sulphur and liquid hydrogen sulphide, with possibly dissolved persulphide. The trisulphide inflames more easily than the crude persulphide, and it burns with a blue flame. R. Schenck and V. Falcke gave 1·70 for the index of refraction with *D*-light.

The chemical characters of the trisulphide are chiefly reducing and sulphurizing, but it also acts as an oxidizing agent. J. H. Walton and L. B. Parsons said that the trisulphide is soluble in benzene, toluene, chloroform, carbon disulphide, ether, and heptanes, while alcohols, ketones, aniline, nitrobenzene, and pyridine decompose it catalytically; I. Bloch and F. Höhn observed that the decomposition with ethyl alcohol is rapid, and with amyl alcohol, explosively violent. Both the di- and trisulphides dissolve in alcohol containing some hydrogen chloride, forming a clear soln. which decomposes rapidly with the evolution of hydrogen sulphide, and the separation of white amorphous sulphur. When the trisulphide is treated with water or hydrochloric acid, the liquid slowly decomposes, becoming turbid owing to the separation of white, amorphous sulphur. Alkali-lye rapidly decomposes the trisulphide; conc. sulphuric acid reacts but slowly with the trisulphide, rapidly with the disulphide, forming white, amorphous sulphur and some sulphur dioxide. In ethereal soln., J. H. Walton and L. B. Parsons concluded that the behaviour is very like that of hydrogen sulphide—copper oleate gave a reddish-brown colloidal precipitate; ferric chloride, a white precipitate which redissolved in excess; stannic iodide, a buff precipitate; silver nitrate, no change; and mercuric bromide, a yellow precipitate; silver oxide, copper oxide, lead dioxide, and mercuric oxide caused a violent decomposition of the trisulphide; the heat evolved was sufficient to ignite the persulphide. Lead oxide, stannic oxide, and magnetite brought about a violent decomposition of the trisulphide. Arsenious oxide, arsenic oxide, ferric oxide, zinc oxide, barium peroxide, and manganese dioxide caused only a slow decomposition. The oxidizing agents potassium permanganate and potassium dichromate were found to decompose the trisulphide rapidly. The permanganate generated sufficient heat to ignite the persulphide. The sulphates of ferrous iron, aluminium, nickel, zinc, and manganese gave a very slow decomposition of the trisulphide. Anhydrous copper sulphate, however, decomposed the trisulphide rapidly, the whole mixture turning dark. The nitrate of aluminium gave only a slow decomposition, while the nitrates of lead, silver, and copper caused a rapid decomposition of the persulphide. Ferric nitrate behaved in a peculiar manner; for a time no visible decomposition took place, and then suddenly an increasingly violent reaction began, as if it were an autocatalytic effect. The chlorides of manganese, sodium, cadmium, ammonium, and lead decomposed the trisulphide only slowly. The chloride of antimony dissolved with the consequent decomposition of the trisulphide. The chlorides of copper and lead turned dark with accompanying decomposition of the trisulphide. The acetate, bromide, and oleate of copper decomposed the trisulphide, rapidly turning dark at the same time. Antimony tri-iodide dissolved in the persulphide. The mixture turned red and decomposed. Massive metals did not decompose the persulphide rapidly. They became coated with the sulphide of the metal and the reaction ceased. Powdered arsenic, antimony and zinc and iron, however, brought about rapid decomposition. It was found that the persulphide was not decomposed by finely ground quartz which had been washed with hydrochloric acid and carefully dried. Neither did boric oxide nor phosphorus pentoxide bring about decomposition. It is to be noted that all copper salts decompose the persulphide as do most lead salts. The trisulphide did not dissolve either copper sulphide or arsenic trisulphide. G. Bruni and A. Borgo state that hydrogen sulphide is insoluble in the persulphides; but J. H. Walton and L. B. Parsons said that the trisulphide dissolves in liquid hydrogen sulphide, forming a liquid which has a pale, straw-yellow colour at room temp. In 5 days crystals of rhombic sulphur separated from the soln., but there was no separation into two liquid layers as was the case when the trisulphide alone was confined in a sealed tube under similar conditions. I. Bloch and F. Höhn said that hydrogen trisulphide dissolves much sulphur at ordinary temp., and the sulphur is precipitated from the soln. when benzene is added. J. H. Walton and L. B. Parsons found that, at 17°-20°, sulphur dissolved until the hydrogen sulphide content of the system was 8 to 9 per cent. J. H. Walton and E. L. Whitford found the solubility of sulphur in hydrogen persulphide—reckoned as per cent. of sulphur not evolved as hydrogen sulphide—to be:

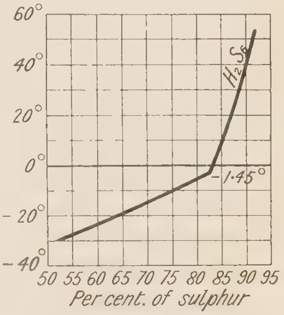
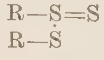


FIG. 41.—Solubility of Sulphur in Hydrogen Persulphide.

	55·3°	35·4°	17·92°	0·05°	−1·45°	−3·75°	−15·42°	−34·72°
Sulphur . .	92·49	89·46	86·77	82·97	82·50	80·71	71·18	53·56

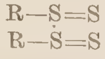
When the data are plotted, Fig. 41, there is a break in the solubility curve near to −1·45° corresponding very closely with hydrogen hexasulphide, H_2S_6. This is taken to mean that at −1·45°, the liquid phase is **hydrogen hexasulphide,** H_2S_6. No other breaks were observed. The hexasulphide is stable below −1·45, but decomposes rapidly at higher temp. The instability of the hydrogen hexasulphide above $-1{\cdot}45°$ explains the necessity for keeping the reaction mixture cold when preparing the yellow oil. The tetrasulphide of hydrogen has not been definitely isolated. H. Mills and P. L. Robinson observed that **hydrogen pentasulphide,** H_2S_5, is produced when ammonium pentasulphide is treated with anhydrous formic acid. The sp. gr. at 16° is 1·67.

The persulphides recall the polyiodides. The organic persulphides are not so readily formed or so stable as the organic periodides, while the reverse appears to be the case with the inorganic per-salts. The element sulphur surpasses iodine in its capacity for forming polyatomic molecules, and this comparison also holds good for the hydrogen compounds. Hydrogen persulphides are well-defined compounds, but corresponding polyiodides are unknown—*the hydrogen diiodide* of the earlier textbooks is no longer considered a chemical individual. According to A. Geuther, the constitution of the polysulphides can be explained on the assumption that sulphur is bivalent, and that hydrogen is tervalent in the disulphide $HS{-}H{=}S$; and in the trisulphide tervalent $S{=}H{-}S{-}H{=}S$, or quinquevalent, $S_2{\equiv}H{-}S{-}H$; and quinquevalent in the tetrasulphide, $S_2{\equiv}H{-}S{-}H{=}S$; and in the pentasulphide $S_2{\equiv}H{-}S{-}H{\equiv}S_2$. This hypothesis, however, has no supporters. E. Drechsel supposed that hydrogen pentasulphide has a sexivalent sulphur atom, $S_2{\equiv}S{=}(HS)_2$, analogous to sulphuric acid, $O_2{\equiv}S{=}(OH)_2$; and, just as sulphuric acid may be regarded as the hydrate of sulphur trioxide, so may hydrogen pentasulphide be regarded as the hydrate of the S_4-molecule. R. Böttger also assumed that because sodium pentasulphide is converted into lead sulphide and sodium thiosulphate when the aq. soln. is boiled with lead hydroxide, it is not to be regarded as Na_2SO_4 with the oxygen replaced by sulphur; and A. Geuther raised a similar objection from his study of the action of silver oxide on finely divided sulphur. W. Strecker obtained methyl trisulphide, $(CH_3)_2S_3$, by the action of methyl sulphate on alcoholic soln. of sodium penta-, tetra-, or tri-sulphide. It is possible that methyl tetra- and penta-sulphides are first formed, and decompose on distillation into the trisulphide. These compounds were previously studied by A. Cahours, and P. Klason. F. Jones also regarded sodium pentasulphide, Na_2S_5, as a tetrathiosulphate, $S.S_4Na_2$, a view favoured by the ease with which it can be converted into the monothiosulphate, $Na_2S_2O_3$, and thence to the sulphate Na_2SO_4. W. Spring and J. Démarteau showed that while the polysulphides behave in accord with the general formula $H_2S.S_n$, their reactions with the alkyl sulphides are best explained by assuming that they possess the formula $H_2S_2.S_n$, in which two sulphur atoms play a *rôle* in the molecule different from the remainder. They consider the higher polysulphides to be merely soln. of sulphur in the disulphides. F. W. Küster and E. Heberlein replied that if this be true, all the polysulphides being essentially salts of hydrogen disulphide, should be hydrolyzed in soln. to the same extent, for the hydrolysis could not be influenced by the mere physical solution of sulphur. They consider that the constitutions of the polysulphides and the polyiodides are analogous, and since it is generally recognized that the latter compounds are best represented by the formula $RI.I_n$, they conclude that the constitution of the polysulphides is best expressed by the formula $R_2S.S_n$. They regarded the polysulphides as salts of complex sulphohydrosulphuric acids: $H_2{=}S{=}S$; $H_2{=}S{=}S{=}S$; $H_2{=}S{=}S{=}S{=}S$; etc. J. S. Thomas and A. Rule added that their study of the polysulphides favours the view that in the polysulphide molecule two atoms of sulphur are in a different state of combination from the remainder. They suggest that the disulphides should be regarded as being derived from the form of hydrogen disulphide analogous to the tautomeric form of hydrogen dioxide. They would thus possess the formula R.S.S.R. From this substance, the higher polysulphides are obtained, not by soln. of sulphur, but by further combination. Thus:



$$\begin{array}{l} R{-}S{=}S \\ \quad\;\vdots \\ R{-}S \end{array}$$

Trisulphide



$$\begin{array}{l} R{-}S{=}S \\ \quad\;\vdots \\ R{-}S{=}S \end{array}$$

Tetrasulphide

According to D. I. Mendeléeff :

> The formation of the polysulphides of hydrogen, H_2S_n, is easily understood from the law of substitution, like that of the saturated hydrocarbons, $C_nH_{2n\ \ 2}$, knowing that sulphur gives H_2S and carbon CH_4, because the molecule of sulphuretted hydrogen may be divided into H and HS. This radicle, HS, is equivalent to H. But substituting this radicle for hydrogen in H_2S we obtain $(HS)HS=H_2S_2$, $(HS)(HS)S=H_2S_3$, etc., in general H_2S_n. The homologues of CH_4, C_nH_{2n+2} are thus formed from CH_4, and consequently the polysulphides H_2S_n are the homologues of H_2S. The question arises why in H_2S_n the apparent limit of n is 5—that is, why does the substitution end with the formation of H_2S_5 ? The answer appears to me to be clearly because in the molecule of sulphur, S_6, there are six atoms. The forces in one and the other case are the same. In the one case they hold S_6 together, in the other S_5 and H_2 ; and, judging from H_2S, the two atoms of hydrogen are equal in power and significance to the atom of sulphur. Just as hydrogen peroxide, H_2O_2, expresses the composition of ozone, O_3, in which O is replaced by H_2, so also H_2S_5 corresponds with S_6.

This hypothesis is favoured by J. J. Blanksma, who represented the sodium polysulphides by the formulæ Na.S.S.Na ; Na.S.S.S.Na ; Na.S.S.S.S.Na ; and Na.S.S.S.S.S.Na ; and also by I. Bloch. I. Bloch also said that the change of colour with change of temp. is possibly explained by an intramolecular change $H_2:S:S \rightleftharpoons HS \vdots SH$, analogous with the keto-enol tautomerism : $H_2:C:O \rightleftharpoons H.C \vdots C.OH$. H. Henstock discussed the electronic structure of hydrogen disulphide.

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§ 11. Sulphoxylic Acid and the Lower Acids of Sulphur

When ethyl sulphide, $(C_2H_5)_2S$, is treated with nitric acid, it is oxidized to the so-called **ethyl sulphoxide,** $(C_2H_5)_2SO$, and to ethyl sulphone, $(C_2H_5)_2SO_2$. Similarly also with **methyl sulphoxide,** $(CH_3)_2SO$, which is also formed when silver oxide acts on methyl sulphobromide, $(CH_3)_2SBr_2$. E. Fromm and J. de Seixas Palma[1] attempted to prepare the so-called *sulphur hydrate*, or **hydrogen sulphoxide,** $S.H_2O$, the hypothetical parent of the organic sulphoxides. If hydrogen sulphoxide has a bivalent sulphur atom, it will be constituted HO.S.H ; and if it has a quadrivalent sulphur atom, $H_2=S=O$. E. Fromm and J. de Seixas Palma found that the action of thionyl chloride on zinc-dust leads to the formation of zinc chloride, sulphur dioxide, and sulphur; a sulphoxide is not formed by treating the mixed products with benzyl chloride. Benzyl disulphide, sulphide, and mercaptan are formed by the action of benzyl chloride on the product of the oxidation of sodium sulphide by hydrogen dioxide, and some sodium sulphide is oxidized to only a small extent yielding sodium sulphate. The action of sulphur on potassium hydroxide and treatment of the product with benzyl chloride leads to the formation of thiobenzoic and benzoic acids together with a small amount of benzyl disulphide. Thiobenzoic acid is oxidized to benzoyl disulphide by potassium ferricyanide in alkaline soln.

No success has attended the effort to make **sulphur monoxide,** SO, the oxide analogous to hydrogen sulphide, SH_2. H. Staudinger and W. Kreis tried unsuccessfully to prepare it by suddenly chilling the vapour of thionyl chloride or bromide from 1000° to −190°. I. Vogel and J. R. Partington tried to make it by heating sulphur sesquioxide to 95° in vacuo. Derivatives are known. For instance, **ethyl sulphone,** $(C_2H_5)_2SO_2$, is obtained from the ethyl sulphoxide by the action of nitric acid, or potassium permanganate; and also by the action of ethyl iodide on potassium ethyl sulphinic acid, $K(C_2H_5)SO_2$. The compound melts at 70° and boils at 248°; similarly with **methyl sulphone,** $(CH_3)_2SO_2$, which melts at 109° and boils at 238°. According to E. Fromm and J. de Seixas Palma, zinc-dust reacts with sulphuryl chloride in ethereal soln., forming zinc chloride and **zinc sulphoxylate,** or **zinc sulphone,** $ZnSO_2$, which is converted into **dibenzylsulphone,** $(C_6H_5.CH_2)_2SO_2$, by treatment with benzyl chloride and a 10 per cent. soln. of sodium hydroxide; benzylsulphonic acid is not formed, as would be the case were the product of the sulphuryl chloride reaction zinc hyposulphite. The syrupy product obtained by evaporating the ethereal soln. of the sulphoxylate reduces indigotin. According to L. Baumann and co-workers, when a soln. of sodium hyposulphite in 40 per cent. formaldehyde is cooled, it deposits a crystalline product which can be separated by fractional crystallization from dil. alcohol into equal parts of **sodium formaldehyde hydrosulphite,** $NaHSO_3.CH_2O.H_2O$, and **sodium formaldehydehydrosulphoxylate,** $NaHSO_2.CH_2O.2H_2O$. The latter compound separates from water in large, transparent, monoclinic prisms, melts at 63°–64°, begins to lose water of crystallization at 120°, at 125° evolves formaldehyde and hydrogen sulphide, and finally leaves a residue of sodium sulphide. Mineral acids decompose it with the formation of sulphur and hydrogen sulphide; alkalies regenerate sodium hyposulphite and formaldehyde, and sodium hydroxide followed by ammonia soln. furnishes disodium hyposulphide and hexamethylenetetramine. **Lead formaldehyde hydrosulphoxylate** is insoluble in water, but dissolves in dil. nitric or in acetic acid to form a strongly reducing soln. The compound can be employed as a reducing agent when warmed in presence of alkalies or sodium hydrogen sulphite and, in these circumstances, gives good results in the conversion of nitro-derivatives into the corresponding amines. According to K. Reinking and co-workers, when the colourless crystals prepared by the interaction of formaldehyde, sodium hydrosulphite, and ammonia, are reduced with zinc-dust and acetic acid, **zinc aminomethylsulphoxylate,** $(NH_2.CH_2.O.SO)_2Zn$, is formed.

I. Vogel and J. R. Partington obtained **sodium ethyl sulphoxylate,** $Na(C_2H_5)SO_2$, by the action of sodium ethoxide on sulphur sesquioxide; and when this is hydrolyzed, by allowing it to stand in contact with its mother-liquid overnight, **sodium sulphoxylate,** Na_2SO_2, is formed. This salt is moderately soluble in cold and more soluble in hot water and sparingly soluble in alcohol. It is practically unattacked by boiling conc. hydrochloric and sulphuric acids, but is attacked by a hot mixture of fuming nitric acid and bromine. The aq. soln. gives a yellow coloration with ferric chloride soln. On exposure to air, the white solid becomes yellowish-brown. It is assumed that the reactions are: $S_2O_3=SO+SO_2$; $SO+C_2H_5ONa=Na(C_3H_5)SO_2$; and $Na(C_2H_5)SO_2+NaOH=Na_2SO_2+C_2H_5OH$. Some of the sulphur monoxide or sesquioxide may react: $SO+2SO_2+C_2H_5ONa$

$=Na(C_2H_5)S_3O_6$; or $S_2O_3+SO_2+C_2H_5ONa=Na(C_2H_5)S_3O_6$; and some pentathionate may be formed by the polymerization of the sulphur monoxide: $5SO+C_2H_5ONa=Na(C_2H_5)S_5O_6$, and $Na(C_3H_5)S_5O_6+NaOH=C_2H_5OH+Na_2S_5O_6$; or $5Na_2S_3O_6=Na_2S_5O_6+Na_2S_4O_6+3Na_2SO_4+3SO_2$. The filtrate from the sodium sulphoxylate has a very unpleasant odour, and contains salts of trithionic, sulphoxylic, and sulphuric acids, and also small quantities of pentathionic and possibly tetrathionic acids. The product of the reaction between sulphur sesquioxide and sodium ethoxide has a strongly alkaline reaction, and under these conditions any tetrathionate and pentathionate which might be produced would probably decompose with the formation of sulphites and thiosulphates, but the absence of the latter indicates that very little, if any, of these substances are produced in the initial reaction. H. Bassett and R. G. Durrant said that the resistance of sodium sulphoxylate to attack by boiling conc. hydrochloric or sulphuric acid is highly improbable, and that the alleged sulphoxylate is more or less impure sodium sulphate, which is precipitated on adding sulphuric acid to a soln. of a sodium compound in absolute alcohol.

A series of salts of sulphinic acid can be obtained by oxidizing dry sodium mercaptide in air: $C_2H_5.SNa+2O=C_2H_5SO_2Na$—**sodium ethylsulphinate**; by the action of sulphur dioxide on zinc alkyl: $(C_2H_5)Zn+2SO_2=Zn(C_2H_5SO_2)_2$—**zinc ethylsulphinate**; and when zinc acts on the chlorosulphonates: $2C_2H_5SO_2Cl+2Zn=ZnCl_2+Zn(C_2H_5SO_2)_2$. According to E. Fromm and J. de Seixas Palma, when sodium hyposulphate reacts with benzyl chloride in a 50 per cent. soln. of sodium hydroxide at ordinary temp., **sodium benzylsulphinate,** $Na(C_6H_5.CH_2)SO_2$, is formed. This is converted into benzyl methyl sulphone, $(C_6H_5.CH_2)(CH_3)SO_2$, m.p. 127°, by boiling with methyl iodide. Similarly, **lead benzylsulphinate,** $Pb(C_7H_7.SO_2)_2$, is obtained by reducing benzylsulphonyl chloride with zinc-dust and alcohol. Both the lead and sodium salts decolorize iodine, but not indigotin, and furnish sulphones when boiled with alkyl halides.

M. Bazlen regarded the compound of formaldehyde with sodium hyposulphite as **sodium hydroxymethanesulphonate,** which is formed along with **sodium hydroxymethanesulphinate,** thus showing that the salt suffers fission with the addition of water as in the case of the dithionates. Sodium hydroxymethanesulphinate reacts with sodium hydrosulphite to form sodium hyposulphite and formaldehyde. The free hydroxysulphonic acids are very unstable, while the hydroxysulphinic acids are stable. Hydroxymethanesulphinic acid is monobasic, whereas hydroxymethanesulphonic acid forms two series of salts—$HO.CH_2.SO_2.R$, and $RO.CH_2.SO_2R$. A. Binz's diformaldehydesulphoxylic acid, $S(O.CH_2.OH)_2$, formed by the action of sodium formaldehydesulphoxylate, or *rongalite*, with formaldehyde and hydrochloric acid, $NaO.S.O.CH_2.OH+HCl+CH_2O=NaCl+S(O.CH_2OH)_2$, is considered by M. Bazlen to be **dihydroxymethylsulphone,** since it readily loses a mol. of formaldehyde. M. Bazlen could not prepare the dibarium salt of hydroxymethanesulphinic acid reported to be obtained from the condensation product of sodium hydroxymethanesulphinate and monomethylaniline.

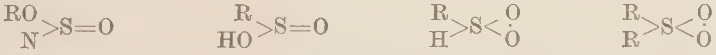
H. Bassett and R. G. Durrant consider the reaction: $3S(OH)_2\rightleftharpoons H_2S+2H_2SO_3$ is improbable because it would be termolecular; and it is more likely that dissimilar molecules are respectively oxidized and reduced. They suggest that in alkaline soln., sulphoxylic acid forms the so-called anhydro-acid, **disulphoxylic acid,** HO.S.O.S.OH, or **pyrosulphoxylic acid,** $2S(OH)_2\rightleftharpoons H_2O+HO.S.O.S.OH$, since many weak acids form pyro-salts in alkaline soln.—*e.g.* boric acid. It is suggested that the sulphoxylic acid is reduced, and the disulphoxylic acid oxidized to pyrosulphurous acid, $H_2S_2O_5$, thus, in symbols: $S(OH)_2+HO.S.O.S.OH\rightleftharpoons H_2S+H_2S_2O_5$. The reversal of this reaction is the first step in Wackenroder's reaction—*vide infra.* Disulphoxylic acid is isomeric with thiosulphuric acid. The behaviour of formaldehydesulphoxylates with the metal salts, shows that in some cases, *e.g.*

with arsenic trichloride, an increase in acidity favours the precipitation of arsenic sulphide instead of arsenic formed when free acid is present. In other cases, *e.g.* with sodium plumbite, an increase in alkalinity favours the formation of lead sulphide, while lead is precipitated as the alkalinity decreases. The reaction $S(OH)_2+HO.S.O.S.OH \rightleftharpoons H_2S+H_2S_2O_5$ would proceed from left to right with a considerable increase in hydrogen ions, for there can be little doubt that sulphoxylic acid would be a very weak acid just as hypochlorous acid is. Alkali should therefore favour the change into sulphide and sulphite, which agrees with the results of the plumbite experiments. In acid soln., high acidity might be expected to favour formation of anhydrosulphoxylic acid at the expense of sulphoxylic acid, and this also would accelerate the change of the latter into hydrogen sulphide and pyrosulphite. The effect of high acidity in favouring precipitation of arsenious sulphide, rather than of free arsenic, would then be intelligible. Increase in acidity would also tend to produce sulphur dioxide at the expense of either sulphurous or pyrosulphurous acid, and this also would hasten the decomposition of sulphoxylic acid. The reaction: $S(OH)_2+H_2S \rightleftharpoons 2S+2H_2O$ occurs with decrease of hydrogen ions, and so will be favoured by acidic conditions. It is this interaction of hydrogen sulphide and sulphoxylic acid which leads to the decomposition of sulphoxylic acid in acid soln. in absence of metals which form insoluble sulphides. Such decomposition could be represented by the summation equation, $2S(OH)_2 \rightleftharpoons H_2SO_3+S+H_2O$.

H. Bassett and R. G. Durrant in their memoir: *The Interrelationships of the Sulphur Acids*, showed that when sulphoxylic acid is liberated by hydrolysis from its association with formaldehyde, it decomposes into sulphurous acid and hydrogen sulphide. If the hydrolysis occurs in the presence of a lead, arsenic, antimony, stannous, bismuth, cadmium, nickel, cobalt, or zinc salt, the sulphide of the metal is precipitated. No acid, other than that present in the soln. owing to hydrolysis, must be added in the case of zinc, nickel, or cobalt, otherwise the precipitate of sulphide fails to appear; and very little must be present in the case of cadmium. With salts of silver, copper, and mercury, reduction to metal occurs. This may occur also with arsenic and probably with antimony or bismuth, especially in absence of much acid, whilst, conversely, a little sulphide may be formed in the case of copper and silver in presence of much acid. Precisely what happens in such cases depends upon the relative rates of the oxidation of sulphoxylic acid to sulphurous acid or of its change into hydrogen sulphide and sulphurous acid. These rates are affected by the conc. of reactants, acidity, and temp. In absence of salts of heavy metals, the hydrogen sulphide acts upon the formaldehyde to some extent to yield trithioformaldehyde, which appears as white crystals or oily drops, and is readily detected by its characteristic smell. The normal interaction of hydrogen sulphide and sulphurous acid leads to the formation of sulphur and polythionic acids. The acid hydrolysis of the formaldehydesulphoxylate occurs rapidly on heating, but is slow at the ordinary temp.; the actual rate depends also upon the acidity. The alkaline hydrolysis is extremely slow, but seems to follow a course similar to that of the acid hydrolysis, yielding sulphide and sulphite. H. Bassett and R. G. Durrant found that the action of formaldehydesulphoxylate on sodium plumbite soln. is slow at the ordinary temp., but more rapid on heating. A mixture of metallic lead and lead sulphide is usually formed, a high conc. of sulphoxylate and high alkalinity being most favourable to the precipitation of lead sulphide. The reduction to metallic lead is due to the sulphoxylate, and not to the formaldehyde. In presence of plumbite, it is the formation of insoluble lead sulphide which accelerates the hydrolysis of the formaldehydesulphoxylate. Sulphur will produce a similar effect by converting the sulphite, formed on hydrolysis of the sulphoxylate, into thiosulphate. Thus it was found that, after an alkaline soln. of formaldehydesulphoxylate had been boiled with sulphur and the polysulphide (much of which was, of course, due to alkaline hydrolysis of the sulphur) removed with lead acetate, the soln. was no longer capable of bleaching methylene-blue. A similar alkaline sulphoxylate soln., after being boiled for the same length of time without sulphur, gave no precipitate with lead acetate and still had a strong bleaching action on methylene-blue. On boiling an alkaline soln. of sodium hydrosulphite to which sodium plumbite has been added, a greyish-black precipitate of lead sulphide and metallic lead is obtained. The same reaction occurs at the ordinary temp., but much more slowly. If the alkaline hydrosulphite soln. is boiled and then cooled to room temp. before the sodium plumbite is added, an immediate black precipitate appears which consists of pure lead sulphide if only small quantities of hydrosulphite and plumbite are used in the experiment. H. Bassett and R. G. Durrant could find no positive evidence in support of the assumption that sulphoxylic acid decomposes: $2S(OH)_2{=}H_2S{+}H_2SO_4$, and $2S(OH)_2{=}H_2S_2O_3{+}H_2O$. They added that if sulphoxylic acid could undergo either of these changes, alkali should promote the changes, since both would correspond to a considerable increase in hydrogen ion. No sulphate is produced when sodium formaldehydesulphoxylate is boiled with a soln. of sodium plumbite; nor is any produced when sodium formaldehydesulphoxylate is hydrolyzed in acidic soln. either alone or in the presence of lead or arsenious salts. If the arsenious sulphide formed had resulted from the decomposition of the thiosulphate, large amounts of sulphate would have been produced. No change was observed when an alkaline soln. of sodium formaldehydesulphoxylate was heated for a long time. If a conc. soln. of hyposulphite is added to conc. hydrochloric acid, sulphur separates at once; but with a conc. soln. of thiosulphate, sulphur does not separate for a long time. If the sulphoxylic acid formed on the hydrolysis of the hyposulphite changed rapidly into thiosulphate, no separation of sulphur is likely to have occurred. The observed separation of sulphur is not due to the presence of a sulphite, for a soln. of an equimolar mixture of sodium pyrosulphite and thiosulphate did not yield any sulphur when added to conc. hydrochloric acid, except after long standing. F. Förster and co-workers assume that the reaction: $2S(OH)_2{=}H_2S_2O_3{+}H_2O$ does occur; and this is supported by the fact, observed by J. Meyer, and K. and E. Jellinek, that sodium hyposulphite, in the absence of air, in neutral or slightly acidic soln., changes quantitatively into sulphite and thiosulphate. The solid salt undergoes a similar change since old specimens contain large proportions of thiosulphate. On the other hand, H. Bassett and R. G. Durrant stated that it is probable that the thiosulphate is not formed directly from sulphoxylic acid, but by a more complex sequence of reactions—*vide infra.* For the smell of sulphoxylic acid, *vide infra,* hyposulphurous acid.

The term sulphoxylic acid was applied by A. Bernthsen to the hypothetical acid H_2SO_2, the parent from which the salts just indicated have been derived. This distinguishes them from the salts belonging to the related hyposulphurous acid, $H_2S_2O_4$—*vide infra.* Sulphoxylic acid, H_2SO_2, was considered by M. Bazlen to be *metasulphoxylic acid,* H_2SO_2, or $HO.SO_2.H$, derived from *orthosulphoxylic acid,* $(HO)_3S.H$, by the loss of a mol. of water.

There are several possible constitutions for compounds with the formula H_2SO_2. For instance, (i) with a bivalent sulphur atom corresponding with an aldehydic or ketonic constitution: RO.S.OM—where R denotes an alkylic or arylic radicle, and M a univalent metal; (ii) another with a quadrivalent sulphur atom, furnishing sulphoxylates or sulphinic acids; and (iii) another with a sexivalent sulphur atom, furnishing sulphinic acids or sulphones:

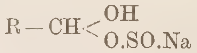


$$\begin{matrix}RO\\N\end{matrix}{>}S{=}O \qquad \begin{matrix}R\\HO\end{matrix}{>}S{=}O \qquad \begin{matrix}R\\H\end{matrix}{>}S{<}\begin{matrix}O\\\dot{O}\end{matrix} \qquad \begin{matrix}R\\R\end{matrix}{>}S{<}\begin{matrix}O\\\dot{O}\end{matrix}$$

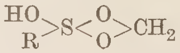
Sulphoxylates Sulphinic acids Sulphones

R. Otto thought that the conversion of the sulphinic acids into sulphones favours the hypothesis that these acids are hydrides and do not contain a hydroxyl group, and that the sulphur atom is sexivalent in the sulphinates. There is, however, some doubt about the constitution of these hypothetical acids which are known only in the form of alkyl or other derivatives. K. Reinking and co-workers, and

M. Bazlen respectively represented the complex aldehydic salt of sulphoxylic acid by the formulæ :



$R-CH<\begin{matrix}OH\\O.SO.Na\end{matrix}$



$\begin{matrix}HO\\R\end{matrix}>S<\begin{matrix}O\\O\end{matrix}>CH_2$

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§ 12. Hyposulphurous Acid

In 1718, G. E. Stahl[1] observed that iron dissolves in sulphurous acid, forming a reddish-yellow liquid ; and C. L. Berthollet observed that no gas is given off when the metal dissolves. A. F. de Fourcroy and L. N. Vauquelin obtained similar results with tin and zinc. C. F. Schönbein and others noticed that when sulphurous acid is electrolyzed, the reddish-brown liquid resembles that obtained by the action of many metals on sulphurous acid, in that both liquids are strong reducing agents, and contain an acid with less oxygen than that contained in sulphurous or rather thiosulphuric acid. E. Schär made more extended observations on this subject. Prior to 1869, it was thought—*e.g.* by E. Mitscherlich—that the acid formed by reducing the sulphurous acid was thiosulphuric acid, $H_2S_2O_3$, while H. Risler-Beunat said that pentathionic acid is formed. Observations were made by M. J. Fordos and A. Gélis, C. Geitner, and A. Harpf, who reported sulphuric, thiosulphuric, trithionic, and pentathionic acids and hydrogen sulphide to be formed. P. Schützenberger showed that *un nouvel acide de soufre* is formed which he called *l'acide hydrosulfureux*—that is, *hydrosulphurous acid.* He also prepared a number of salts of the acid. H. E. Roscoe and C. Schorlemmer, and R. von Wagner preferred the name **hyposulphurous acid,** $H_2S_2O_4$; and they called the salts **hyposulphites**—*vide* thiosulphuric acid. The acid was studied by A. Bernthsen and co-workers, H. Bassett and R. G. Durrant, and by O. Brunck, A. Nabl, etc. The results favour the hypothesis that the molecular formula of the acid is that just indicated—*vide infra.* The arguments in favour of hydrosulphurous or hyposulphurous as a name for the acid have different weights with persons of different temperaments. The writer prefers hyposulphurous acid. The general subject of the hyposulphites was discussed by A. Dubosc,[2] L. A. Pratt, and K. Jellinek.

The preparation of hyposulphurous acid, and the hyposulphites.—As indicated above, hyposulphurous acid is prepared by dissolving iron or zinc in sulphurous acid contained in a closed vessel. P. Schützenberger[3] represented the reaction : $2H_2SO_3+2H_2=(H_2SO_2)_2+2H_2O$. H. E. Causse also prepared hyposulphurous acid in an analogous way by reducing sulphurous acid with zinc, iron, manganese, or copper. F. Bayer used sodium amalgam as the reducing agent. W. Spring showed that the acid is formed along with tetrathionic acid when hydrogen sulphide is passed into sulphurous acid ; L. Maquenne, when sulphurous acid is reduced by hypophosphorous acid ; S. Kapff, by formic acid or sodium formate ; P. Spence and E. Knecht, by titanium trichloride ; G. Scurati-Manzoni, by a copper-zinc couple ; H. Moissan, potassium hydride—but H. Erdmann and H. van der Smissen did not succeed with calcium hydride ; and A. Guerout, by the electrolysis of sulphurous acid. Sulphuric acid is formed at the anode, and hyposulphurous acid is formed at the cathode with a low-current density, and sulphur with a high-current density. C. Luckow also noted the formation of sulphur and hydrogen sulphide. The aq. soln. of the free acid is stable for only a short time. P. Schützenberger obtained it by decomposing the sodium salt with dil. sulphuric or oxalic acid; and R. Englert and F. Becker, by treating a soln. of the calcium salt with sulphuric, oxalic, or phosphoric acid. P. Schützenberger made the sodium salt by the action of zinc on a soln. of sodium hydrosulphite in a well-cooled vessel: $6NaHSO_3+2Zn=2ZnSO_3+2H_2O+2Na_2SO_3+(NaHSO_2)_2$. The greater portion of the sodium sulphite crystallizes out as a complex salt with zinc sulphite. In order to remove the small quantity which still remains in soln., the clear liquid is mixed with 3 or 4 times its bulk of conc. alcohol, and allowed to stand in a well-stoppered flask. The liquid then deposits a second crop of crystals of sodium zinc hyposulphite, and the supernatant liquor when kept in a well-stoppered flask deposits colourless crystals of the hyposulphite. These are pressed between bibulous paper, and dried in vacuo. Another recrystallization may be necessary to remove the last traces of sodium zinc sulphite. L. A. Pratt used a modification of this process; M. Furukawa and K. S. K. Kaisha used nickel or iron salts as catalysts; and W. G. Christiansen and A. J. Norton described a mode of purifying the sodium salt. A. Bernthsen measured the rate of conversion of the sulphur of hydrosulphate into hyposulphite by zinc with soln. containing different proportions of salt in soln. The percentage conversion of the total sulphur into hyposulphite was with soln. containing, per 100 c.c.

$NaHSO_4$.	0·5852	2·3408	3·4094	10·90	17·047	26·97
Conversion .	57·7(16)	57·3(192)	53·7(265)	58·3(18)	53·1(24)	60(¾)

The bracketed numbers refer to the time in hours. M. Bazlen found that the dihydrate, $Na_2S_2O_4.2H_2O$, can be salted out from the soln. by the addition of sodium chloride. The Badische Anilin- und Sodafabrik patented the use of other soluble salts, etc. For instance, sodium nitrite or acetate, chloride of calcium, magnesium or zinc, sodium or ammonium hydroxide. It is better to use soln. as conc. as possible. With 200 c.c. of water and 35 and 40 per cent. of sodium hyposulphite respectively, 98 and 99 per cent. of the hyposulphite was immediately precipitated on adding 60 grms. of sodium chloride. The Farbewerke vorm. Meister Lucius und Brüning showed that instead of zinc and sodium hydrosulphite, a mixture of zinc sodium hydrosulphite and sulphurous, sulphuric, or hydrochloric acid can be used. Other metals more electropositive than zinc were found by E. Grandmougin to be applicable for the reduction. For example, sodium-amalgam may be used, but sodium alone acts too vigorously; calcium can be employed for the reduction.

A. Worsley reduced the supersaturated soln. of sulphurous acid by electrolysis at a low temp., and under press. in the cathode compartment of an electrolytic cell. A non-oxidizing atm. is maintained in the cathode compartment—*e.g.*, by introducing an inert or a reducing gas—and a catalyst—*e.g.*, a zinc salt or a colloid such as gelatin—may be added to the electrolyte. Sulphur dioxide may be continuously introduced into the sulphurous acid soln. during the electrolysis. The soln. of hyposulphurous acid obtained may be used directly as a reducing agent, or the substance to be reduced by hyposulphurous acid may be maintained in close proximity to the cathode, preferably in continuous agitation, during the reduction of the sulphurous acid.

The most satisfactory laboratory method of preparing the sodium salt was found by F. W. Heyl and F. E. Greer to be a process based on those of L. Cassella and Co., and the Manufacture Lyonnaise de Matières Colorantes, namely, the action of sodium hydrosulphite on sodium formaldehydrosulphoxylate, which in turn is obtained by the reduction of commercial hyposulphite with zinc-dust and zinc oxide in the presence of formaldehyde, and recrystallizing the crystals first obtained from water below 70°. It was not found possible to prepare analytically pure anhydrous sodium hyposulphite even by the method from sodium formaldehydesulphoxylate indicated above and salting out the product by means of strong brine. The best results obtained were yields of 55–60 per cent. of the theory with a purity of 80–85 per cent., and neither by recrystallization nor by salting out from air-free aq. soln. in an inert atmosphere could the salt be further purified. J. Volhard obtained the hyposulphite as an intermediate stage in the action of sulphur dioxide on an alkali sulphide. C. F. Schönbein, and P. Schützenberger also obtained sodium hyposulphite at the negative pole during the electrolysis of an aq. soln. of sodium hydrosulphite owing to the reduction symbolized : $2NaHSO_3+H_2\rightleftharpoons Na_2S_2O_4+2H_2O$. A. Villon used a soln. of sp. gr. 1·32 in the cathode compartment. G. Halphen, E. Andreoli, and E. Urbain also employed the electrolytic process. According to E. H. Ekker, the products of the electrolysis are sodium sulphate, water, and either sodium hydrohyposulphite, or a mixture of sodium hyposulphite and free hyposulphurous acid. Working with a cell without diaphragm, he obtained a poor yield by a current of 1·51 amp. passing through a sat. soln. of the sulphite. This diminished after the lapse of another hour. The poor results are due to anodic oxidation of the hyposulphite. K. Elbs and K. Becker used a porous diaphragm, and a cathode of platinum, aluminium, or zinc. They found that at first sodium hyposulphite is formed at the cathode in almost theoretical quantity, but the yield very soon falls off owing to the further reduction of the hyposulphite to thiosulphate, $Na_2S_2O_4+2H=H_2O+Na_2S_2O_3$. It was impossible to prepare solid sodium hyposulphite in this way. When soln. of calcium or magnesium hydrosulphite in water or dil. alcohol are electrolyzed in the same way, a little hyposulphite is formed in soln., but the solid substance which separates out is the neutral sulphite of calcium or magnesium. Zinc hydrosulphite gave similar results. From a conc. soln. of sodium and zinc hydrogen sulphites, however, a solid substance is deposited, about one-quarter of which consists of sodium hyposulphite. Soln. of sodium magnesium and of sodium manganese hydrosulphites gave no solid substance. A. R. Frank showed that in the preparation of soln. of sodium hyposulphite by electrolysis of soln. of sodium hydrosulphite it is necessary to use an almost neutral soln. The presence of free sulphurous acid liberates hyposulphurous acid, which readily decomposes. If this precaution is taken and the current density gradually increased, a good current efficiency can be maintained for a much longer time, and soln. containing 30 to 40 grms. of hyposulphite per litre obtained. Soln. of calcium hydrogen sulphite containing up to 90 grms. of the salt per litre are employed in large quantities in the preparation of cellulose, and the maximum solubility is not 9·3 grms. per litre, as stated by K. Elbs and K. Becker. When a nearly neutral soln. of calcium hydrosulphite containing from 40 to 60 grms. of SO_2 per litre is electrolyzed, the calcium hyposulphite soon begins to crystallize out in silky needles. From 30 to 40 per cent. of the weight of the calcium hydrosulphite used is obtained in the form of the solid hyposulphite, with a current efficiency of 60 to 70 per cent. The dry salt is unstable, about half of it being decomposed after three days' exposure to the air. In the formation of sodium hyposulphite by the electrolysis of sodium hydrosulphite, the electrolysis stops after the soln. contains 3 to 4 per cent. of the hyposulphite. K. Jellinek showed that sodium hyposulphite, in soln. containing hydrogen sulphite, decomposes spontaneously into thiosulphate and hyposulphite and then hydrosulphite, $2Na_2S_2O_4=Na_2S_2O_3+Na_2S_2O_5$; $Na_2S_2O_5+H_2O=2NaHSO_3$. In conc. soln. the rate of decomposition is practically unaffected by the presence of platinum or lead, whilst in dil. soln. the greater part of the change takes place at the surface of a platinized platinum plate. He showed that the stationary condition, in which the conc. of the hyposulphite does not increase, is reached when the rate of formation of hyposulphite by the current is equal to its rate of spontaneous decomposition, from which it follows that the hyposulphite is not reduced electrolytically, and that in order to obtain a high conc. in soln. it is only necessary to increase the rate of formation by applying a large current to a small vol. of soln. The subject was also investigated by K. and E. Jellinek. R. H. McKee and N. Woldman said that, at present, the electrolytic process cannot compete successfully with the zinc process.

The physical properties of hyposulphurous acid.—Free hyposulphurous acid is very unstable. H. Bassett and R. G. Durrant added that freshly acidified hyposulphites have a most unpleasant smell, suggestive of, but differing from, that of hydrogen sulphide, and not unlike a mixture of hydrogen sulphide and sulphur dioxide. The smell recalls that of sewer gas, and it may well be that of sulphoxylic acid. An aq. soln. of hyposulphurous acid, according to its concentration, appears yellow to orange-red. J. Meyer said that it rapidly decomposes into thiosulphuric acid, sulphur dioxide, and hydrogen sulphide. The apparent colour of the acid may be really due to the presence of colloidal sulphur produced by its decomposition. The alleged colour cannot be due to the presence of hyposulphite ions since the alkali salts are colourless; nor is it probable that the colour is produced by the HS_2O_4'-anion, or by the non-ionized molecule since the acid is a strong one. K. Becker did not succeed in collecting the colloidal sulphur in the layer of carbon disulphide when the cathode liquor is shaken with that solvent during the cathodic reduction of sodium hyposulphite. H. Bassett and R. G. Durrant found that when hyposulphurous acid is liberated from its salts, it is hydrolyzed to sulphurous and sulphoxylic acids, and the yellowish-brown coloration which appears is most probably due to a compound, $(HO)_2S.SO_2$, obtained by the co-ordination of one mol. of sulphur dioxide with the sulphur atom of a mol. of sulphoxylic acid. It could also arise directly by a simple intramolecular change. This compound is isomeric with hyposulphurous acid itself, which may be written HO.S.O.SO.OH. When sulphur dioxide is passed into a soln. of sodium formaldehydesulphoxylate, a soln. of precisely the same colour is obtained as from sodium hyposulphite. The properties of the two soln. are similar, and the coloured compound may be the same in the two cases. It is possible, however, that the formaldehyde still remains attached in the one case. It is noteworthy that formaldehyde removes the colour from soln. of all the above sulphur dioxide addition compounds owing to formation of the very stable formaldehydesulphurous acid.

In some cases, very dil. soln. of the acid are fairly stable. M. Berthelot gave 0 to 5·5 Cals. for the heat of formation of the acid in aq. soln. K. Jellinek gave $(2S,3O,H_2O)=H_2S_2O_4+105$ Cals. K. Jellinek found that the electrical conductivity of dil. soln. of the acid can be measured without undue interference by the decomposition of the acid. Thus, 50 c.c. of $\frac{1}{32}N$-$Na_2S_2O_4$ was treated with $\frac{1}{32}N$-HCl, and the conductivity, at 19°, after

Time .	0	20″	40″	1′ 0″	1′ 10″	2′ 40″	6′ 55″	13′ 50″
$k\times10^5$.	557·2	548·0	539·2	532·5	528·2	512·0	479·0	454·5

The corresponding curve represents the rate of decomposition of the acid. Expressing the concentration is gram-equivalents in v litres at 25°:

	8	16	32	64	128	∞
Conductivity .	178	212	234	277	298	422

The temp. coeff. at infinite dilution is 0·017. The ionization constant for $[H^{\cdot}][HS_2O'_4]=K_1[H_2S_2O_4]$ is approximately $K_1=0{\cdot}45$ at 25°; and for $[H^{\cdot}][S_2O_4'']=K_2[HS_2O_4]$, $K_2=0{\cdot}00354$ at 25°. For the heat of formation of the ion $(2S,4O,Aq.)=S_2O_4''$ aq.+177 Cals. For the heat of ionization per gram-atom of sulphur, K. Jellinek gave 89 Cals. The mobility of the S_2O_4''-ion is 69 at 25°. The electromotive force of combinations with a hydrogen electrode, a platinized platinum electrode immersed in well-stirred soln. containing sodium hyposulphite, sulphite, and hydrogen sulphite, is represented by $E=-0{\cdot}245+\cdot\log[S_2O_4''][SO_3'')\,[HSO_3')^4$ at 20° for the normal hydrogen electrode; and for the e.m.f. of the reaction $S_2O_4''+2H_2O+2F=2H^{\cdot}+2HSO_3'$, $E=-0{\cdot}009-0{\cdot}029\log[S_2O_4'']/[H^{\cdot}]^2[HSO_3']^2$ at 20°. From this it is calculated that a soln. containing hyposulphite and hydrogen sulphite ions in normal concentration should be in equilibrium with gaseous hydrogen at two atmospheres pressure, and therefore that the reducing power of such a soln. is very nearly the same as that of gaseous hydrogen. The e.m.f. of the combination measured above increases by 2·27 millivolts per degree rise of temp. From these data the heat of the reaction is readily calculated ; it is $S_2O_4''+2SO_3''+2H_2O+2H^{\cdot}=H_2+4HSO_3'$—13,920 cals. Subtracting the known value, $HSO'_3=H^{\cdot}+SO_3''$ —700 cals., gives $S_2O_4''+2H_2O=H_2+2HSO_3'(-13920-1400=)-15{,}320$ cals. Consideration of the free energy of the reaction between hyposulphites and water leads to the conclusion that they become much less stable as the temp. rises, a rise of 10° increasing the equilibrium press. of hydrogen two and a half times. In alkaline soln. of hyposulphite and sulphite a fairly definite potential is established at a platinum electrode, but the nature of the reaction on which it depends has not been discovered. In soln. of hyposulphite and thiosulphate, or of thiosulphate and sulphite, no definite potential could be observed. The potentials measured were unaffected by the conc. of the thiosulphate.

The chemical properties of hyposulphurous acid and the hyposulphites.—The acid is known only in dil. aq. soln. ; but O. Rössler said that it is more soluble in alcohol than in water. P. Schützenberger, and A. Binz found that aq. soln. of the hyposulphites decompose when warmed, forming only hydrosulphites ; but J. Meyer represented the reaction : $2Na_2S_2O_4+H_2O=Na_2S_2O_3+2NaHSO_3$; and his results for the decomposition at 45°, 60°, and 80° are summarized by the curves shown in Fig. 42. The speed of the decomposition is slow at the start, it then rises to a maximum, and later on slows down. Part of the products of the decomposition react with the undecomposed salt, and consequently the velocity of decomposition is proportional both to the extent of the decomposition, x, and to the quantity of salt left undecomposed, $a-x$; so that $dx/dt=kx(a-x)$. E. Jellinek found k at 0° to be 0·00014 ; at 10°, 0·00023 ; at 20°, 0·00037 ; and at 30°, 0·00063. If $k'=10^5k$, $\log k'=1{\cdot}32+0{\cdot}035\theta$. The decomposition on heating is probably best represented : $2Na_2S_2O_4+H_2O=Na_2S_2O_3+2NaHSO_3$. A. Lumière and L. Seyewetz, and M. Bazlen and A. Bernthsen made some observations on this subject. K. Jellinek studied the decomposition of sodium hyposulphite in soln. of sodium sulphite or hydrosulphite ; and found that it can be represented as a unimolecular reaction $dx/dt=k(a-x)$, where x signifies the amount decomposed at the time t. E. Jellinek found the velocity constant, k, to be, in the presence of

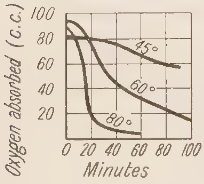


FIG. 42.—The Effect of Temperature on the Decomposition of Neutral Aqueous Solutions of Sodium Hyposulphite.

$NaHSO_5$.	10	15	27	33	15	30 per cent.
k at 18° .	0·00007	0·00031	0·00062	0·00109	—	—
k at 32° .	—	—	—	—	0·00055	0·00250

C. K. Jablczynsky and Z. Warszawska-Rytel found that the rate of decomposition is accelerated by the addition of sodium chloride, and diminished by the addition of a colloid like gum arabic. Dilution retards decomposition. The speed of the reaction corresponds with two reactions of the first order. C. F. Schönbein, P. Schützenberger, and A. R. Frank showed that the decomposition is retarded in the presence of alkalies. Hence, technical operations with hyposulphites are conducted in alkaline soln. whenever possible. Acidic soln. decompose very quickly, for when a soln. of the sodium salt is acidified, it becomes yellow or orange, and much sulphur is separated.

When hyposulphurous acid is liberated from its salts, it is readily hydrolyzed to sulphoxylic and sulphurous acids. H. Bassett and R. G. Durrant summarize the action : $HO.S.O.SO.OH\rightleftharpoons(HO)_2S.SO_2$; by $HO.S.O.SO.OH+H_2O=S(OH)_2+H_2SO_3(\rightleftharpoons H_2O+SO_2)$; and by $S(OH)_2+SO_2\rightleftharpoons(HO)_2S.SO_2$. Thus, two isomeric forms of $H_2S_2O_4$ are assumed. The direct union of two sulphur atoms in $(HO)_2S.SO_2$ indicates that the compound can probably be readily reduced to thiosulphate ; and this is in agreement with K. and E. Jellinek's observation that hyposulphurous and thiosulphuric acids are successive stages in the electrolytic reduction of sulphurous acid. The oxidation of HO.S.O.SO.OH by $(HO)_2.S.SO_2$ is taken to explain the change of the hyposulphite into thiosulphate and pyrosulphite: $HO.S.O.SO.OH + (HO)_2S.SO_2 \rightleftharpoons H_2S_2O_5 + H_2S_2O_3$. The reaction was found by K. and E. Jellinek to be bimolecular, and the rate of change is increased by the presence of hydrosulphites—roughly in proportion to the square of the hydrosulphite concentration—is attributed by H. Bassett and R. G. Durrant to the stabilizing influence of the sulphite. In the presence of acids, there is superposed on these changes the reactions $H_2S + S(OH)_2 \rightleftharpoons 2S + 2H_2O$, and $S(OH)_2 + HO.S.O.S.OH \rightleftharpoons H_2S + H_2S_2O_5$. There is also the possible formation of polythionates by the interaction of hydrogen sulphide and sulphurous acid, or by the decomposition of thiosulphate. F. Förster and co-workers added that polythionates are always formed during the decomposition of hyposulphurous acid. The yellow colour remaining after the disappearance of the yellowish-brown colour of $(HO)_2S.SO_2$, is attributed by H. Bassett and R. G. Durrant to a complex of sulphur dioxide and thiosulphuric acid. The subject was discussed by R. H. McKee and N. E. Woldman. According to H. Bassett and R. G. Durrant, the action of sodium plumbite on the hyposulphites shows that sodium hyposulphite is hydrolyzed slowly in alkaline soln. even at the ordinary temp., and the reactions then observed are the same as those obtained with sodium formaldehydesulphoxylate—both being the reactions of sulphoxylic acid or its decomposition products. If the soln. is boiled before the plumbite is added, a precipitate of lead sulphide free from metallic lead can be obtained in the case of the hyposulphite, because the sulphoxylate is converted into sulphide and sulphite as fast as it is formed. If the plumbite is present during the liberation of the sulphoxylate, some of the latter is oxidized by the plumbite before it is converted into sulphide and sulphite, and so a mixture of lead sulphide and lead is obtained. Alkaline soln. of sulphite give no reaction with plumbite under these conditions, whilst thiosulphate in alkaline soln. gives a very faint reaction. The yellowish-brown colour produced by the acidification of soln. of sodium hyposulphite, with conc. soln., may be similar to that of $0{\cdot}1N$-iodine. The smell of hydrogen sulphide is quite evident directly after acidification, but is soon masked by that of sulphur dioxide. A. Bernthsen and J. Meyer mention that cadmium sulphide is precipitated when hydrosulphite soln. containing cadmium sulphate are acidified, they do not appear to have noticed the hydrogen sulphide itself. Sulphur eventually separates from the acidified soln., but the time which elapses before this occurs may be considerable. The colour persists longest when the acidification has been effected by sulphurous acid. If a conc. sodium hyposulphite soln. is added to conc. hydrochloric acid, a momentary brown colour is produced followed at once by a precipitate of sodium chloride and sulphur.

The dominant quality of hyposulphurous acid, or rather of the hyposulphites, is a strong reducing action. The hyposulphites are readily oxidized. Consequently, in preparation of these compounds, the soln. have to be protected from oxidation by using an atm. of carbon dioxide or hydrogen. A. and L. Lumière and A. Seyewetz found that when a thin layer of powdered anhydrous sodium hyposulphite is exposed to the action of moist **air**, it is completely decomposed in seven days, but is practically stable in a closed vessel or in dry air, the slow changes observed, 10 and 4 per cent. loss of sodium hyposulphite respectively in two months, being due to admission of moisture in removing the daily samples. Soln. of sodium hyposulphite in boiled distilled water in closed vessels decompose at rates varying with the conc.; 25, 10, and 3 per cent. soln. are decomposed in three, eleven, and thirty-seven days respectively. The rate of change is accelerated by rise of temp. or by exposure of the soln. to the air; in the latter case, the relative stabilities are reversed, a 3 per cent. soln. decomposing entirely in one, a 20 per cent. soln. in two days. The decomposition of sodium hyposulphite takes place according to the equation: $3Na_2S_2O_4 = 2Na_2S_2O_3 + Na_2S_2O_6$; $Na_2S_2O_4 + O = Na_2SO_3 + SO_2$, sodium hydrosulphite being formed in aq. soln. The chief product of the reaction is the sulphite. When shaken with air or **oxygen,** P. Schützenberger and co-workers found that soln. of the hyposulphites become yellow or orange, and finally colourless. The yellow coloration is due to the liberation of the free acid. Twice as much oxygen is absorbed as is needed to convert the hyposulphite into hydrosulphite, but J. Meyer found that the quantity absorbed is not quite twice that needed to form the sulphite; and he said that the excess of oxygen is used in carrying the oxidation past the sulphite stage: $H_2S_2O_4+O_2+H_2O=H_2SO_4+H_2SO_3$, and to a small extent: $2H_2S_2O_4+O_2+2H_2O=4H_2SO_3$. P. Schützenberger, and F. J. König and C. Krauch assumed that some hydrogen dioxide is formed; and C. Engler, that a *peroxyhyposulphite*, $H_2S_2O_4.O_2$—an isomer of dithionic acid, or else hydrogen dioxide—is formed:

$$\begin{array}{l}NaSO_2\\NaSO_2\end{array}+\begin{array}{l|l}OH&H\\OH&H\end{array}+\begin{array}{l}O\\O\end{array}=\begin{array}{l}Na.SO_2.OH\\Na.SO_2.OH\end{array}+H_2O_2$$

Mild oxidizing agents—*e.g.* silver salts—normally oxidize hyposulphite to sulphite, but with mol. oxygen, J. Meyer said that during the oxidation of the hyposulphites, sulphite and sulphate, as well as thiosulphate, and dithionate may be formed; and the sulphate and sulphite would be in equimolar proportions were it not for disturbances produced by the hydrolysis of the hyposulphite by the acid formed during the oxidation. H. Bassett and R. G. Durrant added that with soln. containing sufficient sodium carbonate to neutralize the acid formed, the atm. oxidation of hyposulphite proceeds smoothly as a unimolecular reaction.

A. and L. Lumière and A. Seyewetz found that *chloral* and *quinol* exert no protective action on soln. of sodium hyposulphite. The influence of a number of other substances on the stability of the soln. is as follows, where the first bracketed number represents the number of grams per litre; and the number in brackets after "days" refers to the percentage amount of hyposulphite undecomposed, in the other cases, all was decomposed in the time stated: *Sodium hydroxide* (10–100), 5 days; *sodium carbonate* (2), 4 days; (100), 11 days; *potassium carbonate* (5–200), 8 days; ammonia (10–200 c.c.), 4 days; *normal sodium phosphate* (5), 3 days; (50), 6 days; (100), 24 days; *sodium hydrophosphate* (50), 5 days; (100), 7 days; *sodium silicate,* (25), 5 days; (100), 23 days (0·9); *acetaldehyde* (30 c.c.), 28 days (5·9); (100 c.c.), 21 days; *formaldehyde* (50 c.c.), 28 days (14·9); (200), 28 days (8·1); *acetone* plus sodium sulphite (5+15), 5 days; (20+60), 7 days; (40+120), 4 days; *aniline* (100), 4 days; *methylamine* (100), 4 days (0·9); *trioxymethylene* plus sodium sulphite (10+1), 28 days (26·5); (50+3), 28 days (24·4); *hexamethylenetetramine* (100), 28 days (24·4).

J. Meyer found that **hydrogen dioxide** oxidizes hyposulphites in acidic or alkaline soln., forming sulphates, and a small proportion of dithionates. The reaction was examined by A. Wangerin and D. Vorländer, and F. S. Sinnatt. The hyposulphites were found by A. Bernthsen to be oxidized by **iodine** to sulphates. Brotherton and Co. represented the reaction with sodium hyposulphite and **potassium iodate:** $3Na_2S_2O_4+4KIO_3+2KI=3I_2+3Na_2SO_4+3K_2SO_4$. W. Spring found **sulphur** to be without action on sodium hyposulphite; and L. Tschugaeff and W. Chlopin observed that a warm soln. of sodium hydroxide and hyposulphite attacks sulphur to a very slight extent—*vide infra,* tellurium. A. Binz showed that while the hyposulphite has no action on **sodium sulphide,** it reacts vigorously with **sodium polysulphides:** $Na_2S_2O_4+Na_2S_n+H_2O=NaS.SO.OH+NaS.SO_2.OH+Na_2S_{n-2}$, but these products immediately decompose giving off hydrogen sulphide; with sodium polysulphide and hydroxide: $Na_2S_2O_4+Na_2S_2+4NaOH=2Na_2SO_3+2Na_2S+2H_2O$; also $2Na_2S_2O_4+2Na_2S_2+2NaOH=2Na_2S+3Na_2S_2O_3+H_2O$; and with an excess of polysulphide: $Na_2S_2O_4+Na_2S_n+4NaOH=2Na_2S_2O_3+Na_2S+Na_2S_{n-3}+2H_2O$. A. Binz and W. Sondag found that the reaction in alkaline soln. can be represented: $Na_2S_2O_4+Na_2S_2O_3+4NaOH=3Na_2SO_3+Na_2S+2H_2O$. W. Spring showed that if **hydrogen sulphide** be passed into a feebly acidified soln. of potassium hyposulphite, the liquid becomes hot, sulphur is precipitated, and the liquid no longer decolorizes indigo; if the soln. be neutralized with potassium carbonate, no sulphur is deposited, and potassium thiosulphate, precipitable by alcohol, is formed. L. A. Tschugaeff and V. A. Chlopin observed that **tellurium** is attacked by a soln. of sodium hydroxide containing the hyposulphite warmed on a water-bath. The liquid becomes violet and then colourless, and on cooling, it deposits sodium telluride. Similarly also with **selenium,** but the reaction does not takes place so readily. J. Meyer found that like the sulphites, hyposulphites reduce **selenium dioxide** to selenium, but the reaction is more energetic. If the soln. of selenium dioxide is very dilute, colloidal selenium is formed. O. Brunck said that **selenous acid** is reduced to selenium by hyposulphites, but not so with **selenic acid ;** both **tellurous acid,** and **telluric acid** are completely reduced to tellurium, and with very dilute soln., colloidal tellurium is formed.

J. Meyer found that in the absence of air, alkaline or neutral soln. of **nitrates** are not reduced by hyposulphites, but if air be present, sodium hydrosulphite is formed, and this reacts with the nitrate forming amidosulphonic acid: $KNO_2+3NaHSO_3+H_2O=NaOH+2NaHOS_4+NH_2.SO_2.OK$. With acidified soln., however, there is a vigorous reaction with the evolution of nitrous oxide and nitrogen. A. Lidoff found that some hydroxylamine is formed, and he represented the reaction with potassium nitrite: $2KNO_2+2H_2SO_2+2H_2O=K_2SO_4(NH_2OH)_2.H_2SO_4$. O. Brunck showed that in a feebly acidified soln. of **arsenious acid,** amorphous, brown arsenic is formed; in neutral soln., the precipitation occurs on allowing the mixture to stand for a short time; but in a soln. made alkaline with alkali carbonate, no precipitation occurs. W. Farmer and J. B. Firth noticed that arsenic tritasulphide, As_3S (*q.v.*), is produced by the action of sodium hyposulphite on certain **arsenic salts.** A little arsenic disulphide is probably always formed at the same time. With a feebly acidified soln. of **antimony trichloride,** antimony is precipitated, and if the hyposulphite be in excess, antimony trisulphide mixed with sulphur is formed. An acidified soln. of **potassium antimonate** behaves similarly; and with a hot neutral or alkaline soln. antimony is precipitated. A dil. soln. of **potassium bismuth tartrate** furnishes colloidal bismuth; with a soln. of **bismuth chloride,** a reddish precipitate is formed, and this soon blackens forming bismuth mixed with a little sulphide, if the hyposulphite be in excess, bismuth sulphide is precipitated; and **bismuth hydroxide** suspended in water is slowly reduced to the metal.

E. H. Ekker represented the reaction with **potassium ferricyanide** by the equation: $Na_2S_2O_4+2K_3FeCy_6=2SO_2+2K_3NaFeCy_6$. The reaction was studied electrometrically by C. del Fresno and L. Valdes. The action of sodium hyposulphite in neutral or acidic soln. on **formaldehyde** furnishes a complex **sodium formaldehydohyposulphite,** $Na_2S_2O_4.2CH_2O.4H_2O$; and a similar product is obtained by the action of zinc and an acid on the complex with sodium sulphite and formaldehyde. This subject was studied by A. Binz,[4] L. Baumann and co-workers, H. Schmid, A. Pelizza and L. Zuber, L. Descamps, K. Reinking and co-workers, M. Müller, Farbwerke vorm. Meister Lucius und Brüning, Badische Anilin- und Sodafabrik, E. Glimm, E. Knoevenagel, A. Osann, M. Bazlen, E. Fromm and J. de Seixas Palma, and C. Schwartz and co-workers. According to M. Muntadas, an insoluble, stable, pulverulent formaldehyde-zinc hyposulphite compound is formed by boiling a mixture of sodium hydrosulphite, formaldehyde, zinc-dust and sulphuric acid. The following reaction is stated to take place: $2(NaHSO_3+CH_2O)+3Zn+2H_2SO_4=2(ZnSO_2+CH_2O)+ZnSO_4+Na_2SO_4+2H_2O+H_2$. The insoluble hydrosulphite compound is filtered off, washed, dried, and passed through a sieve. It can be employed advantageously for many of the purposes for which less stable salts of the hyposulphites are used. Soln. of **indigo** and other colouring agents are bleached by hyposulphites. The reaction with indigo was studied by C. F. Schönbein,[5] E. Schär, P. Schützenberger and C. Risler, J. E. Tulleken, A. Müller, M. Müller, F. Tiemann and C. Preusse, A. Bernthsen and A. Drews, A. Binz and co-workers, R. Möhlau and co-workers, A. Wangerin and D. Vorländer, and W. Vaubel. The reduction of **azo-compounds** by hyposulphites was studied by E. Grandmougin,[6] O. Fischer and S. Eilles, and H. Franzen and P. Stieldorf; of **diazonium salts,** by E. Grandmougin; of **nitro-compounds,** by E. Grandmougin,[7] P. Goldberger, P. Aloy and co-workers, and F. Gaess; of **nitroso-compounds,** by E. Grandmougin; of **organic arsenic compounds,** by P. Ehrlich,[8] A. Bertheim, and L. Benda; and O. Fischer and A. Fritzen, of **triphenylmethane** dyes. P. Schützenberger [9] observed that **anthraquinone** in alkaline soln. gives a red precipitate with hyposulphites; and L. Beaudet, that it does not decompose **sugars.**

P. Schützenberger [10] reported that hyposulphites precipitate cuprous hydride when added to a soln. of **copper sulphate;** J. Meyer said that colloidal copper, not the hydride, is formed—*vide* **3**. 21, 6. J. E. Myers and J. B. Firth showed that the product is either pyrophoric copper, associated with a little cuprous sulphide or mainly the sulphides. O. Brunck represented the reactions: $CuSO_4+Na_2S_2O_4=Cu+Na_2SO_4+2SO_2$; and $Cu+2Na_2S_2O_4=CuS+Na_2S_2O_5+Na_2SO_3$. Hyposulphites reduce **cupric chloride** to **cuprous chloride,** and slowly reduce the latter to copper; with ammoniacal soln. of cupric salts, a copper-mirror is formed. He found that at temp. up to 30°, a soln. of cupric chloride is reduced by sodium hyposulphite to cuprous chloride which is permanent in the presence of an excess of cupric chloride: $6CuCl_2+Na_2S_2O_4+4H_2O=3Cu_2Cl_2+2NaCl+2H_2SO_4+4HCl$; with increasing amounts of hyposulphite, the cuprous chloride is reduced to copper: $Na_2S_2O_4+Cu_2Cl_2=2Cu+2NaCl+2SO_2$, and finally converted to cupric sulphide: $Cu+Na_2S_2O_4=CuS+Na_2SO_4$. At temp. from 50° to 75°, the final product, if cupric chloride is present in excess, is mainly cuprous sulphide, which is converted into cupric sulphide by excess of sodium hyposulphite. J. Meyer found that if a soln. of a hyposulphite be slowly added to a dil. soln. of **silver nitrate,** colloidal silver is formed—*vide* **3**. 23, 10. Unlike A. Seyewetz and J. Bloch, O. Brunck found that the precipitate always contains sulphide. J. B. Firth and J. Higson found that with up to 6 per cent. soln. of sodium hyposulphite, the action on **silver chloride** is very slight, the product of the reaction being mainly silver sulphide; and with increasing conc. of the hyposulphites, the reaction furnishes a mixture of silver and of some silver sulphide: $Na_2S_2O_4+2AgCl=2NaCl+2Ag+2SO_2$ which may proceed in stages: $Na_2S_2O_4+AgCl=NaCl+NaAgS_2O_4$, and the intermediate sodium hyposulphite is then reduced: $NaAgS_2O_4+AgCl=NaCl+2Ag+2SO_2$. For conc. up to 6 per cent. hyposulphite the maximum reaction occurs at 35°, and for higher conc., the maximum reaction occurs at 50°. As the temp. is further increased the extent of the reaction rapidly diminishes until at 80° it is very slight. The product of the action of sodium hyposulphite soln. on a soln. of silver chloride in sodium thiosulphate is entirely sulphide, 6 grms. of original silver chloride being completely precipitated as sulphide by 6 grms. of hyposulphite: $AgCl+Na_2S_2O_3=NaAgS_2O_3+NaCl$, followed by $2NaAgS_2O_3+Na_2S_2O_4=Na_2SO_4+Na_2S_4O_6+Ag_2S$. If the silver chloride is dissolved in excess of ammonia soln. the silver compound is quantitatively reduced to metallic silver. Silver is quantitatively precipitated as the finely-divided metal from an ammoniacal soln. of silver nitrate. G. Scutari-Manzoni found that a soln. of silver chloride and ammonia or potassium cyanide is reduced to metal by sodium hyposulphite. Soln. of **gold salts** are reduced to metal; and with dil. soln., M. Gröger obtained purple-red colloidal gold—*vide* **3**. 23, 10.

O. Brunck found that a neutral soln. of a **zinc salt** is not changed by hyposulphites in the cold, but when boiled with an excess of hyposulphite, zinc sulphide is formed: $ZnS_2O_4+2Na_2S_2O_4=ZnS+2Na_2S_2O_5+SO_2$; similarly also in the presence of acetic acid. No visible change occurs when sodium hyposulphite is added to a dil. soln. of **cadmium sulphate,** but with a conc. soln. a white precipitate of a complex salt is formed; with a feebly acidified soln. of cadmium sulphate, there is first formed cadmium hyposulphite which then decomposes to the sulphide: $CdSO_4+3H_2S_2O_4=CdS+H_2SO_4+2H_2SO_3+3SO_2$; sodium thiosulphate may also be produced: $CdSO_4+3Na_2S_2O_4=CdS+2Na_2SO_3+Na_2SO_4+3SO_2$. According to J. Meyer, a dil. soln. of **mercuric nitrate** forms with the hyposulphite a colloidal soln. of mercury; and O. Brunck, and N. A. Orloff found that in neutral or acidic soln., all the mercury is precipitated as metal; and if an excess of hyposulphite is present, some mercury sulphide is formed.

O. Brunck found that soln. of **aluminium salts,** in the absence of free acid, when boiled with sodium hyposulphite, precipitate incompletely aluminium hydroxide mixed with sulphur; at ordinary temp. neutral soln. of **indium salts** give no precipitate, but when boiled, yellow indium sulphide is incompletely precipitated as a decomposition product of the hyposulphite. With acidic soln., no precipitate is formed. Neutral soln. of **thallium salts,** in the cold, give a reddish-brown, violet, or black precipitate of thallous sulphide. The precipitation is incomplete. With feebly acidified soln., a red precipitate is formed immediately; and with strongly acidified soln., no precipitation occurs.

According to C. R. Fresenius, sulphuric acid or hydrochloric acid soln. of **titanic oxide** are coloured an intense red by hyposulphites, and the colour gradually fades to reddish-yellow, and yellow, and finally becomes colourless. O. Brunck said that the colour does not appear with alkaline soln. Presumably the reduction of **titanium tetrachloride** is symbolized: $TiCl_4 + Na_2S_2O_4 \rightarrow 2TiCl_3 + 2NaCl + 2SO_2$; but E. Knecht found that sulphurous acid is reduced to hyposulphurous acid by titanium trichloride: $2TiCl_3 + 2NaCl + 2SO_2 = 2TiCl_4 + Na_2S_2O_4$. The equilibrium conditions were studied by K. Jellinek, and B. Diethelm and F. Förster. O. Brunck found that the behaviour of **zirconium salts** towards hyposulphites is very like that with aluminium salts. No precipitate is formed with acidified soln., and with a boiling neutral soln., white zirconic hydroxide mixed with sulphur is formed. No precipitation occurs with neutral or acidified soln. of **germanium salts.** A feebly-acidified, conc. soln. of **stannous chloride** gives a voluminous, white precipitate when treated with a 10 per cent. soln. of sodium hyposulphite; stannous hyposulphite appears to be formed, and with an excess of the hyposulphite, a soluble double salt is produced; and this easily decomposes into tin and sulphur. If a dil. soln. of stannous chloride be used, stannous sulphide is precipitated; **stannic chloride** is completely precipitated as yellow tin sulphide by hyposulphite. When sodium hyposulphite is added to a neutral soln. of a lead salt, a yellowish-white precipitate is formed which rapidly turns red, then brown, and finally black. The precipitation is complete. It is assumed that lead hyposulphite is first precipitated; and this rapidly passes into the sulphide.

K. Jellinek showed that **chromic salts** are not reduced by hyposulphites to chromous salts. O. Brunck found that, at ordinary temp., **chromic acid,** and **chromates** are immediately reduced by hyposulphites to chromic salts in neutral or in alkaline soln. A feebly acidified soln. of **ammonium molybdate** furnishes brown molybdenum sulphide; a neutral soln. is coloured brownish-red owing to the formation of ammonium sulphomolybdate. A feebly acidified soln. of **ammonium tungstate** is coloured deep blue; the neutral soln. is not changed. V. Kohlschütter and H. Rossi, and O. Brunck found that soln. of **uranium salts** are reduced by hyposulphites to uranous salts. A greyish-green precipitate of uranous sulphate is formed when a hyposulphite is added to a yellow soln. of **uranyl acetate or nitrate.**

O. Brunck found that **manganous salt** soln. suffer no visible change when treated with hyposulphites; acidified or neutral soln. of **permanganates** are immediately reduced to manganous salts; and in alkaline soln. the dioxide is precipitated. C. F. Mohr found that **ferric salts** are immediately reduced to ferrous salts: $Na_2S_2O_4 + Fe_2(SO_4)_3 + H_2SO_4 = 2FeSO_4 + 2NaHSO_4 + 2SO_2$; and O. Brunck found that when a neutral soln. of a **ferrous salt** is warmed, black iron sulphide is precipitated. Neutral or ammoniacal soln. of **nickel salts** give a precipitate of nickel sulphide; and **cobalt salt** soln. behave in an analogous manner.

The addition of hyposulphite to a dil. soln. of **platinic chloride** gives a yellow coloration which becomes dark red owing to the formation of platinous chloride. A colloidal soln. of platinum is not formed, but the metal is soon precipitated.

Neutral or acidified soln. of **palladium salts** are, at once, completely reduced to metal mixed with some sulphide.

The hyposulphites are used in dyeing and colour printing;[11] in bleaching sugar;[12] and in some analytical work. The so-called *rongalite* and *hydraldite* are commercial names for complexes of sodium hyposulphide and formaldehyde used as discharges for cotton.

The constitution of hyposulphurous acid and the hyposulphites.—P. Schützenberger[13] first gave $NaHSO_2$ as the formula of sodium hyposulphite, but A. Bernthsen showed that the formula is $NaSO_2$ or a multiple of this $(NaSO_2)_n$. P. Schützenberger assumed that the reactions: $2SO_2+Zn+H_2O=H_2SO_2+ZnSO_3$; and $3NaHSO_3+Zn=ZnSO_3+H_2O+Na_2SO_3+NaHSO_2$ show that the sodium salt contains only one atom of sodium in accord with the formula HO.SO.H; C. W. Blomstrand also explained the reducing properties of the acid by assuming that it has the aldehydic structure HO.SO.H, and when the acid is oxidized, it becomes HO.SO.OH. The formulæ H_2SO_2 and $NaHSO_2$ were supported by W. A. Dixon, J. Grossmann, M. Prud'homme, and L. Baumann and co-workers. A. Bernthsen found that in the oxidation of the hyposulphite, one atom of sulphur in the hyposulphite requires 3 atoms of iodine to form sulphuric acid; and hence the anhydride of hyposulphurous acid must be S_2O_3, not SO; also, analysis shows that the atomic proportion Na : S is as 1 : 1; and this agrees with the empirical formula $(NaSO_2)_n$. This also agrees with M. Bazlen's analysis. This is supported by the formation of the zinc salt, ZnS_2O_4, when zinc dissolves in sulphurous acid, $Zn+2SO_2=ZnS_2O_4$, observed by A. Bernthsen; and by the action of sulphur dioxide on granulated zinc in a cooled flask containing absolute alcohol. J. Meyer found that if the oxidation of sodium hyposulphite be conducted with an ammoniacal soln. of cupric sulphate, two stages can be recognized; for, in the cold, sodium sulphite is formed, and at a higher temp., in the presence of ammonium chloride, sodium sulphate. A. Bernthsen showed that the consumption of oxygen agrees with the equations: $Na_2S_2O_4+O=Na_2S_2O_5$, followed by the oxidation of the pyrosulphite: $Na_2S_2O_5+O_2+H_2O=2NaHSO_4$. H. Moissan said that the synthesis of the hyposulphite by the action of the alkali or alkaline earth hydride on sulphur dioxide proceeds according to the reaction: $2KH+2SO_2=K_2S_2O_4+H_2$; and not as formulated by P. Schützenberger: $2KH+2SO_2=2KHSO_2$. H. Erdmann and H. van der Smissen did not confirm H. Moissan's observation in the case of calcium hydride.

While chemical analysis does not distinguish between the formula $NaSO_2$ or $Na_2S_2O_4$—or still higher multiples—the probability is that the acid is dibasic because all the other oxy-sulphur acids are dibasic with respect to sodium. This is confirmed by observations on the electrical conductivity of soln. of sodium hyposulphite basicity rule—1. 15, 13—and also with the assumption that with complete ionization the factor *i*—1. 10, 15—approaches 3, in accord with $Na_2S_2O_4 \rightleftharpoons 2Na^{\cdot}+S_2O_4''$, and not with $NaSO_2 \rightleftharpoons Na+SO_2'$. This conclusion is also in harmony with measurements of the f.p. of dil. soln. of sodium hyposulphite.

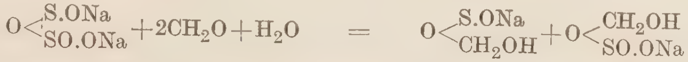
J. Meyer, and C. Engler deduced a graphic formula on the assumption that hyposulphurous acid is formed by the reduction of asymmetric sulphurous acid:

$$\begin{array}{l} H.SO.\vdots\,\boxed{OH + H} \\ H.SO.\vdots\,\boxed{OH \quad\; H} \end{array} \quad = \quad 2H_2O+\begin{array}{l} H.SO_2 \\ H.SO_2 \end{array}$$

and that when oxidized, dithionic acid is formed:

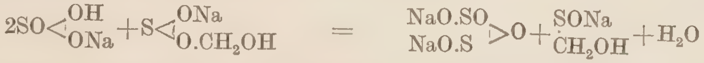
$$\begin{array}{l} H.SO_2 \\ H.SO_2 \end{array}+O_2 \quad = \quad \begin{array}{l} HO.SO_2 \\ HO.SO_2 \end{array}$$

M. Bazlen suggested that hyposulphurous acid is a disulphinic acid $H.SO_2.SO_2H$, with a S.S-linkage. This explains its formation by the reduction of sulphurous acid. Powerful oxidizing agents, such as iodine, cause rupture of the S.S-linking with production of sulphate in place of the expected dithionate. Under certain conditions, manganese dioxide, potassium permanganate, or nickel oxide cause the formation of dithionic acid, which is also obtained from sulphurous acid; in alkaline soln., however, dithionate is either not obtained or produced only in subordinate amount from sulphite. A. Binz, however, argued that when methyl sulphate is treated with sodium hyposulphite, methyl hyposulphite is first formed, $(CH_3)_2SO_4+Na_2S_2O_4=Na_2SO_4+(CH_3)_2S_2O_4$; and that this decomposes into dimethylsulphone: $(CH_3)_2S_2O_4=SO_2+(CH_3)_2SO_2$. He therefore recommended an asymmetrical formula $Na.SO.O.SO_2.Na$. This agrees with the action of sodium hyposulphite on formaldehyde—previously indicated—which results in the scission of the molecule at the oxygen junction between the two sulphur atoms:



$$O<\substack{S.ONa\\SO.ONa}+2CH_2O+H_2O = O<\substack{S.ONa\\CH_2OH}+O<\substack{CH_2OH\\SO.ONa}$$

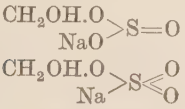
and the formation of hyposulphite from sodium hydrosulphite and sodium formaldehydosulphoxylate is represented by the equation:



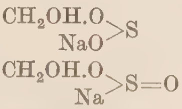
$$2SO<\substack{OH\\ONa}+S<\substack{ONa\\O.CH_2OH} = \substack{NaO.SO\\NaO.S}>O+\substack{SONa\\CH_2OH}+H_2O$$

This also agrees with the assumption that hyposulphurous acid is a mixed anhydro-acid with an asymmetrical structure, and derived from a mol. each of sulphurous and sulphoxylic acids. It might then be anticipated that the hydrolysis of sodium hyposulphite should furnish the sodium salts of these two acids: $Na_2S_2O_4+H_2O=NaHSO_3+NaHSO_2$; but this is not the case. This means that the oxygen-bridge in the hyposulphites is very stable, and that it resists hydrolysis. The stability of the oxygen-bridge is supposed to be an effect of the unsaturated state of the sulphur atom of the sulphoxylate. The effect of mild oxidizing agents—*vide supra*—supports the asymmetrical structure.

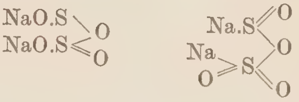
There are different views as to the way the sodium is combined in the molecule; and this, in turn, is dependent on the active valencies of the sulphur atoms. Thus, there are the alternate forms:



Aldehydosulphite



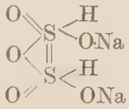
Aldehydosulphoxylate

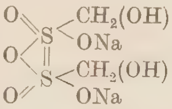


Hyposulphite

where the metal is attached to sulphur by an oxygen-bridge when the sulphur is assumed to have a low valency, and it is attached directly to the sulphur atom when the higher valency is postulated.

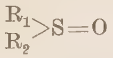
H. Bucherer and A. Schwalbe said that the sodium hyposulphite obtained by salting out from an aq. soln. always contains at least one mol. of constitutional water, and they assign to it the first of the following formulæ:





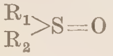
They say that it has two hydrogen atoms replaceable by a metal; that it is neutral towards litmus; and that with formaldehyde it forms an additive product which condenses with the amines. The second of these above formulæ is not probable because the evidence shows that the CH_2O is united to sulphur by an oxygen-bridge; and the formula does not explain the scission of the molecule into two unequal parts, hydrosulphite and sulphoxylate, as previously indicated. J. E. Orloff, and H. Remy have made some speculations on the constitution of the hyposulphites.

The tetrahedral structure of the sulphoxides has been supported by the observations of H. Phillips,[14] and S. Sugden. If the unsymmetrical sulphoxides

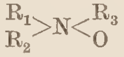


$$\begin{matrix}R_1\\R_2\end{matrix}\!>\!S{=}O$$

contain a plane of symmetry passing through the two radicles R_1 and R_2, and bisecting the double bond, they should be optically inactive, but if the double bond is semi-polar, as in optically active methyl-ethylamine oxide of J. Meisenheimer, the two structures are analogous :

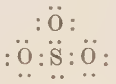


$$\begin{matrix}R_1\\R_2\end{matrix}\!>\!S{=}O$$

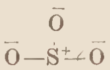


$$\begin{matrix}R_1\\R_2\end{matrix}\!>\!N\!<\!\begin{matrix}R_3\\O\end{matrix}$$

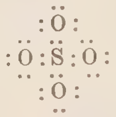
G. Oddo [15] discussed the constitution of the oxy-acids of sulphur in the light of his theory of mesohydry. H. Burgarth, and T. M. Lowry has discussed the **electronic structure of the oxy-acids of sulphur.** The latter said that the S″-ion has the electronic structure $:\underset{..}{\overset{..}{S}}:$, and that the double negative charge of the sulphide-ion would be distributed between sulphur and oxygen in the S′—O′-ion, or $:\underset{..}{\overset{..}{S}}:\underset{..}{\overset{..}{O}}:$, of the hypothetical acid H_2SO ; whilst the SO_2″-ion, $:\underset{..}{\overset{..}{O}}:\underset{..}{\overset{..}{S}}:\underset{..}{\overset{..}{O}}:$, or O′—S—O′-ion of the acid H_2SO_2 has both negative charges on oxygen, and none on sulphur. While the ion of H_2SO-acid is incapable of existence, the ion of the H_2SO_2-acid has a low order of stability. Stable ions begin to be formed only when the central sulphur atom acquires a positive charge as in the SO_3″-ions :



or



ions of the sulphites ; or the SO_4″-ions



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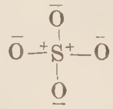
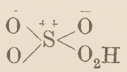


ions of the sulphates. The sulphur series of acid ends when four oxygen atoms are linked to the central atom. Persulphuric acid of the formula H_2SO_5 is known, but it is to be regarded as a monosulphonic derivative of hydrogen dioxide :



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§ 13. The Hyposulphites

M. Prud'homme[1] prepared **ammonium hyposulphite,** $(NH_4)_2S_2O_4$, by saturating a soln. of ammonium hydrosulphite, of sp. gr. 1·357, with a slight excess of ammonia, and agitating it in the cold with zinc turnings. Half the salt is converted into insoluble zinc diamminosulphite, and half into soluble ammonium hyposulphite. The filtrate is free from zinc. The yield is 96–98 per cent. of the theoretical where

6 mols. of ammonium hydrosulphite form 2 mols. of **ammonium hydrohyposulphite,** presumably $(NH_4)HS_2O_4$, one mol. of normal ammonium hyposulphite, 2 mols. of zinc sulphite, and one mol. of the diamminosulphite. The ammonium hydrohyposulphite was not isolated. H. Moissan[2] obtained **lithium hyposulphite,** $Li_2S_2O_4$, by the action of lithium hydride on sulphurous acid. The reaction is slow at room temp., but proceeds quickly at 50°. Some lithium sulphide is formed at the same time. The preparation of **sodium hyposulphite,** $Na_2S_2O_4$, has been described in connection with the acid. The salt obtained from the aq. soln. at ordinary temp. is the *dihydrate*, $Na_2S_2O_4.2H_2O$, and it is very unstable. The dehydration of the hyposulphite without decomposition, said K. Jellinek, *ist von allen Hyposulphitoperationen die schwierigste.* The anhydrous salt is obtained by heating the dihydrate above its dehydration temp., 52°, either alone or under conc. alkali-lye, sodium chloride soln., or alcohol, removing the mother-liquor by suction and drying in vacuo. These operations were the subject of patents by the Badische Anilin- und Sodafabrik, the Chemische Fabrik von Heyden, and the Farbwerke vorm. Meister Lucius und Brüning. It is everywhere necessary to keep the salt alkaline in order to retard its decomposition; and also to keep the salt agitated to prevent the formation of clots. The Badische Anilin- und Sodafabrik obtained the anhydrous salt by the action of sulphur dioxide on sodium, a lead-sodium, or a mercury-sodium alloy, suspended in alcohol or ether; M. Billy said that the sulphur dioxide reacts with sodium confined under alcohol, but not under ether; and E. Grandmougin said that dry sulphur dioxide reacts with sodium only when traces of moisture are present. H. Moissan obtained the hyposulphite by the action of sodium hydride on sulphur dioxide. K. Jellinek found that 100 grms. of water dissolved 21·1 grms. of the anhydrous salt at 20°; and 100 grms. of soln. at 1°, 10°, and 20° contain respectively 12·85 grms., 14·40 grms., and 16·46 grms. of $Na_2S_2O_4$ with the dihydrate as the solid phase. The solubility curve is plotted in Fig. 43. The ice-line extends to the eutectic at —4·58° with 1·93 molar per cent. $Na_2S_2O_4$. The solubility curve, with the dihydrate as solid phase, extends to the transition point at 52° and 2·8 molar per cent. of $Na_2S_2O_4$. M. Bazlen found that the transition temp. is 52° under conc. alcohol, and is not much altered if the salt be under a soln. of sodium chloride or sodium hyposulphite. Above 52°, the anhydrous salt is the solid phase. Metastable soln. are represented by the curves *CBA*. The curve *CB* represents the solubility of the anhydrous salt below the transition temp. when the anhydrous salt is more soluble and less stable than the hydrate. The curve *BA* represents the solubility of the dihydrate above the transition temp., where it is more soluble and less stable than the anhydrous salt.

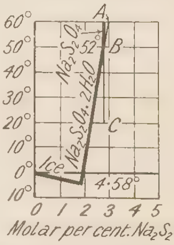

Fig. 43.—Solubility of Sodium Hyposulphite.

P. Schützenberger described sodium hyposulphite as a salt which appears in colourless, acicular crystals which, when dried in vacuo, crumble to a powder. A. Bernthsen and M. Bazlen found that the dry salt can be kept many days in air without change, but when kept in a closed vessel for some months, it gradually loses its reducing power. In moist air, the salt is quickly oxidized, and becomes hot. The Badische Anilin- und Sodafabrik added that its decomposition into thiosulphate and pyrosulphite is hindered if the crystals are washed with water mixed with alcohol or a ketone and dried immediately in vacuo. A. Bernthsen and M. Bazlen showed that the crystals melt when dehydrated at a dull red-heat, and burn with a blue flame with the evolution of sulphur dioxide. P. Schützenberger said that when the salt is heated it develops water, sulphur, and sulphur dioxide, and leaves a residue of sodium sulphide and sulphate. M. Bazlen said that the heat of transformation of the dihydrate into the anhydrous salt is negative; and that the heat of dehydration is also negative. R. Robl observed no fluorescence with the salt in ultra-violet light. K. Jellinek found that soln. containing an eq.

of the salt, $Na_2S_2O_4$, in v litres of water had the eq. conductivity, λ ohms, and the degree of ionization, α, at 0°:

v	2	8	16	32	64	128	256	512	1024	∞
λ	48	76	85	91	98	103	107	110	112	122
α	0·393	0·627	0·697	0·746	0·803	0·844	0·877	0·902	0·918	1·000

and the molar conductivity, μ mhos, at 25°:

v	4	8	16	32	64	128	256	512	∞
μ	77	84	90	96	99·5	103	107	111	120
α	0·642	0·700	0·750	0·800	0·829	0·858	0·892	0·917	1·000

Analogous values for the degree of ionization were obtained from the f.p. of the soln. P. Schützenberger found that the salt is soluble in dil. alcohol, but not in conc. alcohol. As shown by A. Bernthsen and M. Bazlen, when the aq. soln. is acidified, it becomes red, and sulphur is formed. R. Wagner found that when the aq. soln. has been kept for some time, it contains thiosulphate. J. Meyer said that the aq. soln. slowly decomposes at 45°, and at higher temp., rapidly: $2Na_2S_2O_4+H_2O=Na_2S_2O_3+2NaHSO_3$. The general reactions have been indicated in connection with hyposulphurous acid. According to L. Eymer, dry sodium hyposulphite with 70–95 per cent. alcohol has a greater reducing action on dyed cotton than water; but the addition of alcohol to the aq. soln. does not increase its reducing action. Fires have occurred in the transport of the dry salt owing to the heat generated by the action of moisture.

According to H. Moissan, when dry sulphur dioxide mixed with its own vol. of hydrogen is passed at ordinary temp., and under ordinary or reduced press., over potassium hydride, for about 50–60 hrs., white **potassium hyposulphite,** $K_2S_2O_4$, is formed. M. Bazlen showed that if the hydrated salt be extracted with boiling acetone, and treated with methyl alcohol, the white salt is precipitated and can then be dried in vacuo just over 52°. The Badische Anilin- und Sodafabrik obtained the *trihydrate*, $K_2S_2O_2.3H_2O$, in sulphur-yellow needles, by treating a soln. of potassium hydrosulphate and sulphur dioxide with zinc-dust; adding milk-of-lime to the partially solid mixture; adding alcohol to the filtered liquor; and shaking the cooled liquid precipitate with alcohol. The anhydrous salt is fairly stable, but the hydrate decomposes in a short time. H. Moissan prepared **rubidium hyposulphite,** $Rb_2S_2O_4$, by the action of sulphur dioxide under diminished press. on rubidium hydride; **cæsium hyposulphite,** $Cs_2S_2O_4$, was obtained in a similar way.

H. Moissan prepared **calcium hyposulphite,** CaS_2O_4, by the action of sulphur dioxide, at 900 mm. press., on calcium hydride. The action is very slow at ordinary press. H. Erdmann and H. van der Smissen added that *die Resultate Moissans nicht bestätigen.* The Badische Anilin- und Sodafabrik mixed a soln. of sodium hyposulphite at 50°–70° with a conc. soln. of calcium chloride, and stirred the liquid for some time. A soln. of calcium hydrosulphite can be converted into the hyposulphite by methods described in connection with the hyposulphites generally, and the neutral salt can be precipitated by the addition of calcium hydroxide. A. R. Frank, and K. Elbs and K. Becker discussed the preparation of this salt by the electrolysis of a soln. of calcium hydrosulphite. The calcium hyposulphite obtained by precipitation was found by M. Bazlen to be the *hemitrihydrate*, $CaS_2O_4.1\frac{1}{2}H_2O$; it furnishes white, acicular crystals which do not completely lose their water at 120°. The Farbwerke vorm. Meister Lucius und Brüning said that the complex salt with aldehyde is fairly stable. H. Moissan made **strontium hyposulphite,** SrS_2O_4, by the action of a current of sulphur dioxide under press. on strontium hydride at 70°.

The Badische Anilin- und Sodafabrik obtained **magnesium hyposulphite,** MgS_2O_4, by the method employed for the calcium salt; and A. R. Frank, by the electrolytic reduction of a soln. of magnesium hydrosulphite—a process which K. Elbs and K. Becker found to give poor yields. H. Moissan did not make this salt by the action of sulphur dioxide on the hydride; but M. Billy found that when magnesium in the presence of a neutral solvent, like ether or light petroleum, is exposed to the action of sulphur dioxide, magnesium hyposulphite is formed. It is said that traces of the metallic ethoxide and hydride are first formed; the latter reacts with the sulphur dioxide to form the hyposulphite regenerating hydrogen, which converts a fresh portion of the metal into the hydride. An almost quantitative yield, and a more stable product, was obtained by the Badische Anilin- und Sodafabrik from a mixture of 750 litres of alcohol, 250 litres of water, 270 kgrms. of zinc-dust, and 470 kgrms. of sulphuric acid, well-stirred at a temp. above 40°—best at 60°–75°—washing the product with conc. alcohol, and drying in vacuo at 60°–70°. M. Bazlen obtained the hydrated salt, contaminated with some sulphite by passing sulphur dioxide into water agitated with zinc-dust at 30°–40°; and allowing the oily liquid to crystallize. A similar process was employed by the Chemische Fabrik von Grünau Landshoff und Meyer. According to V. von Lang, the acicular crystals are rhombic and have the axial ratios $a:b:c=1{\cdot}0176:1:0{\cdot}5694$. M. Bazlen said that the salt is very soluble in water and is liable to form supersaturated soln.; the Farbenfabrik vorm. F. Bayer also found it to be easily soluble in aq. ammonia. The salt rapidly loses its reducing power when exposed to air; and when kept in closed vessels it loses sulphur dioxide.

M. Bazlen observed that a soln. of zinc hyposulphite forms complex salts with the alkalies and alkaline earths. The Farbenfabrik vorm. F. Bayer obtained soluble **ammonium zinc hyposulphite,** by reducing an alkali hydrosulphite with zinc-dust in the presence of ammonium chloride. The Badische Anilin- und Sodafabrik obtained **sodium zinc hyposulphite,** $Na_2S_2O_4.ZnS_2O_4$, as a crystalline precipitate by adding sodium chloride, nitrite, or acetate to a soln. of zinc hyposulphite; the water of crystallization is expelled at 100°–110°. It is also made by adding zinc chloride to a soln. of sodium hyposulphite. M. Bazlen said that this salt is produced as a white solid when sulphurous acid soln. of sodium hydrosulphite is reduced with zinc-dust. The product is impure. Similar remarks apply to other modes of preparation in which zinc and sodium salts are involved—*e.g.* of the Farbwerke vorm. Meister Lucius und Brüning, the Chemische Fabrik von Griesheim Elektron, and G. Münch. The double salt is said to be fairly stable; less easily dissolved by water than the component salts; easily soluble in ammonia. The Farbenfabrik vorm. F. Bayer obtained what was considered to be **sodium zinc sulphitodihyposulphite,** $Na_2SO_3.2ZnS_2O_4$, by treating a warm soln. of zinc hyposulphite with sodium hydrosulphite. M. Bazlen, the Badische Anilin- und Sodafabrik, and the Farbwerke vorm. Meister Lucius und Brüning prepared **potassium zinc hyposulphite** by the method employed for the sodium salt. It is insoluble in alcohol. M. Bazlen found that **calcium zinc hyposulphite** is more soluble than its components, and J. Grossmann thought that the soln. of the double salt was an easily soluble *calcium hydrohyposulphite.* O. Brunck prepared **sodium cadmium hyposulphite,** $Na_2S_2O_4.2CdS_2O_4$, as a white crystalline precipitate, by mixing conc. soln. of cadmium sulphate and sodium hyposulphite. P. B. Sarkar prepared **gadolinium hyposulphite** in an impure state. O. Brunck found that **stannous hyposulphite** is obtained as a white crystalline precipitate by adding stannous chloride in neutral soln. to a soln. of sodium hyposulphite. The precipitate is soluble in an excess of the sodium salt; if the stannous chloride soln. be acidic, stannous sulphide is precipitated as indicated above. According to W. Farmer and J. B. Firth, **sodium arsenious hyposulphite,** $Na_3As(S_2O_4)_3$, was formed as a cream-white powder by agitating a mixture of 2·75 grms. of sodium hyposulphite in a cold soln. of 2·75 grms. of sodium arsenate in 3 c.c. of water. The granular precipitate was washed five times by decantation with methylated alcohol and four times with benzene, and dried in a quartz dish in vacuo over sulphuric acid for 24 hrs. When a small quantity of the product is strongly heated in a bunsen flame, a brown and a yellow sublimate is formed and a garlic odour developed. If cautiously heated, the product first turns brown and, when more strongly heated, gives a brown and a yellow sublimate as before. When a small quantity of the product is treated with dil. hydrochloric acid, sulphur dioxide is evolved and brown arsenic tritasulphide, As_3S, is formed.

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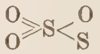
§ 14. Sulphur Sesquioxide

The hypothetical *hyposulphurous anhydride*, S_2O_3, has not been prepared, but R. Weber[1] reported what he called *dithionoxyd*, or **thionyl oxide**, $(SO)_2O$, or **sulphur sesquioxide**, S_2O_3, to be formed by the action of dried flowers of sulphur, added in small quantities at a time, on an excess of sulphur trioxide. Drops of a deep blue colour sink to the bottom and solidify immediately ; the temp. during the operation must be kept at about 15°, for if it is lower, the anhydride no longer remains liquid ; if higher, the substance decomposes. When about a gram of sulphur has been added, the anhydride, which should have remained perfectly colourless, is poured off, and the solid bluish-green crystalline mass is freed from any impurities that remain by gentle heat. The bluish-green crystalline mass decomposes at ordinary temp. giving off sulphur dioxide, and leaving, when sheltered from moisture, perfectly dry sulphur. In presence of water it is immediately decomposed, forming sulphuric, sulphurous, and probably thiosulphuric acids. Absolute alcohol and anhydrous ether decompose it with deposition of sulphur. The sesquioxide is insoluble in sulphur trioxide, but it is very soluble in a mixture of sulphur trioxide and ordinary sulphuric acid, and the solution when kept in sealed tubes remains blue for many weeks, but gradually becomes green, then brown, and finally assumes the ordinary hue of oil of vitriol. The brown liquid is produced by the addition of weaker acid or of sulphur to the blue soln. ; the former is the much less stable of the two. The blue sesquioxide dissolves in a mixture of sulphuric acid containing a fifth or less of sulphur trioxide, with formation of the brown liquid ; in an acid containing more than a fifth sulphur trioxide a blue liquid is produced, while in an acid weaker than sulphuric acid the sesquioxide is completely decomposed. The sulphur sesquioxide prepared by R. Weber is an indifferent oxide, which cannot be regarded as the anhydride of an acid. H. Piotrowsky observed its formation in the action of hydrazine on sulphur dioxide.

The blue substance has been in part discussed in connection with colloidal sulphur (*q.v.*). In 1804, C. F. Bucholz obtained a blue distillate by heating a mixture of sulphur and sulphuric acid in a retort. F. C. Vogel obtained it by the action of sulphur on sulphur trioxide and noted that by using different proportions of sulphur and of its trioxide, brown, green, and blue products are obtained. The brown substance contains the largest proportion of sulphur, and the blue substance the least. When the mixtures are heated, they evolve sulphur dioxide, and sometimes a little sulphur trioxide while sulphuric acid remains behind—this shows that some water was also present. In contact with water, these coloured products are resolved, with the evolution of much heat, into sulphur, and sulphurous and sulphuric acids. The blue product forms sulphates with the alkalies and alkaline earths while much sulphur dioxide is evolved. J. S. C. Schweigger showed that the coloured substances can be readily converted one into the other, and that all of them are readily decomposed, forming sulphur, etc. H. Rose observed that the blue liquid reacts violently with ammonia gas, forming a carmine-red soln. which produces a white mass of ammoniacal salts having red spots here and there. When extracted with water, sulphur remains undissolved. According to N. W. Fischer, when the vapour of anhydrous sulphuric acid is passed into a tube containing dry sulphur and the tube sealed, the blue product is formed at particular places, and is immediately decomposed, forming sulphur dioxide and trioxide. If a trace of moisture be present, there may be a slight evolution of gas, and a liquid is formed which is first brown, then green, and finally blue. In a few days, the liquid becomes colourless. When the tube is opened, sulphur dioxide escapes with violence, and the remainder may form a blue liquid. Sulphuric acid itself dissolves very little sulphur. J. J. Berzelius, and W. Stein supposed that these coloured liquids are soln. of sulphur, and a similar conclusion was drawn by J. Biehringer and W. Topaloff. C. F. Wach obtained the coloured liquids by allowing alternate layers of well-dried flowers of sulphur and sulphur trioxide, in sealed glass tubes, to act on one another at 16°–19°. For the brown product, sulphur and sulphur trioxide were employed in the gravimetric proportions 2 : 10; for the green liquid, 1·5 : 10; and for the blue liquid, 1 : 10.

P. P. von Weimarn regarded the blue sulphur sesquioxide as a soln. of sulphur in the trioxide. R. Auerbach said that sulphur dissolves in pyrosulphuric acid as S_2-mols., without the formation of S_2O_3; and he found that the f.p. of soln. of sulphur in pyrosulphuric acid indicated that the sulphur is in the diatomic form, and is less polymerized—*i.e.* more highly dispersed—than it is in most organic solvents where it is octatomic. No indication of the formation of sulphur sesquioxide was obtained.

I. Vogel and J. R. Partington obtained a substance of approximately constant composition—S_2O_3—by adding either sulphur to liquid sulphur trioxide or *vice versa.* The mol. wt. in soln. could not be determined because it was at once decomposed by all the solvents tried, including phosphorus oxychloride. The sesquioxide begins to decompose at about 70°, and decomposition is complete at 95°. The residue then melts to a liquid which has all the characteristic properties of sulphur. When the sesquioxide is treated with water, it is immediately decomposed, forming a pale yellow soln., which immediately decomposes, forming a turbid soln. by the separation of sulphur. The filtered soln. contains sulphuric and trithionic acids together with indications of tetrathionic, pentathionic, and sulphurous acids. It was suggested that the decomposition first proceeds: $S_2O_3=SO+SO_2$; that some of the monoxide polymerizes and forms pentathionic acid: $5SO+H_2O=H_2S_5O_6$; and that another portion produces sulphoxylic acid: $SO+H_2O=H_2SO_2$. The formation of trithionic acid may take place in accord with the equation: $S_2O_3+SO_2+H_2O=H_2S_3O_6$, or $SO+2SO_2+H_2O=H_2S_3O_6$. The trithionic acid then reacts with nascent sulphur, forming tetrathionic and pentathionic acids. There is a violent reaction with ether and the product decomposes with the separation of sulphur, and the formation of a yellow soln.; and a similar result was obtained with absolute ethyl alcohol. With an anhydrous soln. of sodium ethoxide, there is a vigorous reaction, forming a yellowish-brown liquid and a yellow crystalline solid—sodium ethyl sulphoxylate, $Na(C_2H_5)SO_2$. Sulphur sesquioxide dissolves in oleum with the formation of a deep blue soln. identical with that produced by the addition of sulphur. A soln. of indigo in conc. sulphuric acid or of indigo-carmine in water is partially decolorized; in no case could complete decoloration be effected even by the addition of comparatively large quantities of the substance. A similar reaction takes place with strongly ammoniacal copper sulphate soln., the decoloration being only partial. I. Vogel and J. R. Partington concluded that pure sulphur is insoluble in pure sulphur trioxide, although combination occurs with the formation of sulphur sesquioxide, which is also practically insoluble. It is only in the presence of small quantities of water that the substance dissolves to a blue soln. The blue liquid is a *molecular* soln. of sulphur sesquioxide in oleum, whilst the other coloured liquids produced by the dissolution of sulphur in fuming sulphuric acid of certain strengths are mixtures of colloidal soln. of sulphur and mol. soln. of sulphur sesquioxide. The compound was studied by W. Prandtl and P. Borinsky who represented its constitution by



$$\substack{O\\O}{>}S{<}\substack{O\\S}$$

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§ 15. Sulphur Dioxide and Sulphurous Acid

It was shown in connection with the history of sulphur that the fumes from burning sulphur were used from the earliest times for disinfecting purposes. Paracelsus,[1] in his *De naturalibus rebus*, said that " crude sulphur has the property of bleaching red colours with its fumes; it turns red roses into white ones." A. Libavius, 1595, obtained what he called *spiritus sulfuris acidus* by leading the fumes from burning sulphur into a vessel full of water; and he observed that when this soln. is exposed to air it is converted into an acid identical with that obtained by distilling vitriol, or treating sulphur with nitric acid. J. B. van Helmont observed that the gas extinguished a flame, and he regarded it as a *spiritus sylvestris*. He said:

> Every seed of burnt sulphur is destroyed by the flame and it is thereby transformed into a gas or a *spiritum sylvestrem*, which by reason of the properties of its own concrete or composed body, is an antidote against the pest.

G. E. Stahl, 1702, distinguished between sulphurous and sulphuric acids and called them respectively *acidum volatile*, and *acidum fixum*, although some later writers —*e.g.* H. Boerhaave—said that the two acids are the same. G. E. Stahl supposed sulphurous acid to come between sulphur and sulphuric acid; and said that sulphur in burning looses phlogiston and forms sulphuric acid, and that the sulphuric acid unites with some undecomposed sulphur to form sulphurous acid; hence sulphurous acid was considered to be *phlogisticated sulphuric acid*. A circumstance, added H. Cavendish, "which I think shows the truth of this, is that if oil of vitriol be distilled from sulphur, the liquor which comes over will be the volatile sulphureous acid." J. Priestley, 1775, prepared sulphur dioxide, and collected it over mercury. He called it *vitriolic acid air*. In opposition to the phlogiston theory, A. L. Lavoisier, 1777, proved that the difference between sulphurous and sulphuric acid is not due to the different proportions of contained phlogiston, but rather to the degree of oxidation of the sulphur. He called the gas from burning sulphur *gaz acide sulfureux*, and the soln. in water *acide sulfureux* in contrast with the more highly oxidized *acide sulfurique*. The gas was analysed by J. L. Gay Lussac in 1808, and by J. J. Berzelius in 1811, and 1818; and its salts were studied by A. F. de Fourcroy and L. N. Vauquelin.

Sulphur dioxide occurs in the gaseous exhalations of volcanoes and fumaroles as indicated in connection with hydrogen sulphide. The presence of sulphur dioxide in the gases associated with volcanic activity is common. The gas is found in the grottoes of Santa-Fiora, Sienna, Ætna, Stromboli, Bourbon, etc., as well as in the volcanoes of Java, Andes, etc. It also occurs in the springs of water near active volcanoes. The occurrence of sulphur dioxide in the fumes from Vesuvius was noted by H. Davy;[2] T. Monticelli and N. Covelli said that the gas is produced in fissures and holes only when atm. air is in contact with red-hot lava; and F. Hoffmann, that hydrogen sulphide, not sulphur dioxide, was emitted by flakes of fresh scoriæ when broken. Hence, added G. Bischof, the presence of sulphur dioxide presupposes atm. air, and it can be supposed to be formed at such depths as are accessible to air, whether the sulphur is furnished by sulphur or by sulphides. L. Ricciardi attributed the formation of sulphur dioxide in volcanic gases to the interaction of silica with calcium and magnesium sulphates, either jointly or singly, and the sulphur trioxide which separates is decomposed into sulphur dioxide and oxygen: $SiO_2+MgSO_4=MgSiO_3$ (enstatite)$+SO_3$; $SiO_2+CaSO_4=CaSiO_3$ (wollastonite)$+SO_3$; and $SiO_2+CaSO_4+MgSO_4=MgCaSiO_4$ (monticellite)$+2SO_3$. An artificial mixture of granite with magnesium and calcium sulphates evolved sulphur dioxide. On the other hand, R. Bunsen attributed the formation of sulphur dioxide to the oxidation of hydrogen sulphide, and to the decomposition of the sulphates of the alkalies and alkaline earths at a high temp. R. T. Chamberlin also observed that ferrous sulphate and basic ferric sulphate are decomposed by heat: $2FeSO_4=Fe_2O_3+SO_2+SO_3$; and $Fe_2S_2O_9=Fe_2O_3+2SO_3$. He also noticed that some rocks give off relatively large amounts of sulphur dioxide when heated. G. C. Wittstein noted sulphur dioxide in the waters of Alle Prese, Grisons. Sulphurous acid has been found in numerous mineral waters by F. Boudet, and others. G. Witz observed that the existence of sulphur dioxide as a normal constituent of the air of towns is shown by the fact that placards coloured with red-lead, posted in situations where they are protected from the sun and rain, became gradually decolorized, whereas similar placards exposed under similar conditions in country air retain their colour unimpaired. The decolorized placards are found to contain lead sulphate and lead sulphite, the lead dioxide in the red-lead having been converted into the former, and the monoxide into the latter. This decolorization of the red-lead takes place much more rapidly in shop windows where gas is burnt. Sulphurous acid was also found to occur in hail, snow, and especially hoar frosts in the neighbourhood of towns. L. Coniglio found alkali sulphites to be products of the normal activity of Vesuvius. G. H. Bailey found a maximum of 32·2 mgrms. of SO_2 per 100 c. ft. of the air of Manchester and Salford, and a minimum of 1·0 mgrm. per 100 c. ft.—*vide* **8**. 49, 1. H. Wislicenus observed that the air in different parts of the Tharandt Forest, ten kilometres from any source of smoke, showed the presence of sulphur dioxide inside the forest, though in less quantity than at the edges. C. le Blanc reported it to occur in some natural waters, though its tendency to oxidation to sulphuric acid renders it an unlikely occurrence except in very special cases.

Preparation.—Sulphur dioxide is formed when sulphur burns in air or oxygen. Some sulphur trioxide is produced at the same time, as indicated in connection with the chemical properties of sulphur. If air be employed, the sulphur dioxide is of course accompanied by nitrogen from the air. The nitrogen does no harm in some of the technical applications of the gas. Numerous furnaces have been devised for burning sulphur; many of these are provided with automatic feeders, and agitators. These are described by W. Wyld,[3] and others in works devoted to the manufacture of sulphuric acid. The gas is also obtained by roasting many metal sulphides in air. In 1818, T. Hills and U. Haddock obtained a patent in England for producing sulphur dioxide by roasting pyrites for the manufacture of sulphuric acid; but, according to E. Sorel, this was done by a French manufacturer, M. d'Artigues, in 1793. N. Clement also made experiments on the subject in 1810. The burning of pyrites on a large scale is done by heating iron pyrites, copper pyrites, zincblende, etc., in special kilns or burners, so arranged that the heat of oxidation is utilized for maintaining the process without extraneous fuel. As shown by A. Scheurer-Kestner, G. Lunge and F. Salathé, and D. Pierson, some sulphur trioxide is formed in this operation—*vide supra*, the oxidation of sulphur. There are also burners arranged for roasting the spent oxide of gas-works so as to convert the sulphur into sulphur dioxide; hydrogen sulphide may also be burnt to sulphur dioxide in special burners. Some sulphide ores are roasted in heaps in the open air without any regard for the contained sulphur. The ultimate object is the extraction of the metal. The damage to health and vegetation is, however, so great that the nuisance has been stopped by legal enactments. For the same reason, the noxious vapours—mainly sulphur dioxide—in many manufacturing districts have to be treated for the removal of sulphur dioxide and trioxide before the "smoke" is permitted to escape into the atmosphere. The various methods for treating acid-smoke, smelter-fumes, hydrogen sulphide, etc., for the recovery of the sulphur in the gas as sulphur dioxide, are described in special treatises—*e.g.* by C. A. Hering, C. Schnabel, W. Wyld, etc. F. Siemens converted hydrogen sulphide into sulphur dioxide by burning it admixed with air at 280°–320° in contact with a catalyst containing a metal capable of combining with sulphur—*e.g.* copper, nickel, or iron—and an oxygen carrier—*e.g.* vanadium, chromium, or molybdenum. L. H. Diehl devised a process for recovering the 1·5 per cent. of sulphur—chiefly as calcium sulphide—in blast-furnace slag, by blowing hot air through the fused slag as it is tapped from the furnace. The air which escapes at about 950° contains about 10 per cent. of sulphur dioxide by vol. Sulphur dioxide is also formed when other sulphur compounds are heated in air—*e.g.* when carbon disulphide is burnt; and as U. Collan and others have shown, when coal gas is burnt.

Sulphur dioxide is also produced when the oxides of many metals—manganese, zinc, lead, mercury, etc., are heated with sulphur, or with sulphur compounds of the same metals. Thus, P. Berthier used pyrolusite, $MnO_2+2S=MnS+SO_2$; or $2MnO_2+S=SO_2+2MnO$; and R. F. Marchand, a mixture of copper oxide and sulphur: $2CuO+2S=Cu_2S+SO_2$. F. Stolba heated sulphur with ferrous sulphate, $FeSO_4+2S=FeS+2SO_2$, and, as a by-product, obtained ferrous sulphide for the manufacture of hydrogen sulphide; T. Terrell utilized the reaction: $2FeSO_4+2S+3O=Fe_2O_3+4SO_2$, and employed the ferric oxide as a pigment; the reaction of sulphur with cupric sulphate was stated by H. Schiff to proceed more easily than with ferrous sulphate. C. Brückner made a special study of the action of sulphur on the sulphates. F. Martin and O. Fuchs found that the alkaline earth sulphates are reduced to sulphides when heated with iron, and the reduction occurs at a lower temp. than when coal is substituted for the iron. The reduction is complete in half an hour at 750° for calcium sulphate; at 850° for strontium sulphate; and at about 950° for barium sulphate. In the presence of insufficient iron and at about 150° higher, a rapid evolution of sulphur dioxide takes place.

The best conditions for this are, for calcium sulphate the mixture $16CaSO_4+15Fe$, giving 80 per cent. of the theoretical yield of sulphur dioxide; for strontium sulphate the mixture $9SrSO_4+8Fe$, giving an 88·9 per cent. yield. These reactions lead to the formation of well defined ferrites, $3CaO,2Fe_2O_3=Ca_3Fe_4O_9$; $2SrO,Fe_2O_3=Sr_2Fe_2O_5$; and $BaO,Fe_2O_3=BaFe_2O_4$. Too little iron leads to the formation of alkaline-earth sulphide, too much iron gives also iron sulphide. Sulphur dioxide is also evolved by heating the alkaline-earth sulphates with iron sulphide; this can be carried out commercially by using pyrites to which has been added a little iron oxide. L. Moser purified the gas by the fractional distillation of the liquefied gas.

Sulphur dioxide is produced in the thermal decomposition of conc. sulphuric acid, as when the acid is dropped into a red-hot platinum flask packed with pumice-stone. Sulphur dioxide is also formed when many sulphates are heated, for the sulphur trioxide first given off breaks up into oxygen and the gas in question. The Verein Chemischer Fabriken Mannheim used iron oxide as catalyst at about 900°—*vide supra*, sulphur. H. S. Elworthy obtained it by heating a mixture of sodium sulphide with calcium or sodium sulphate in a converter furnace in air, when all the sulphur is given off as sulphur dioxide; and L. P. Basset heated a mixture of calcium sulphate with alumina and powdered coal. Sulphur dioxide is also formed when sulphuric acid is heated with sulphur: $2H_2SO_4+S=3SO_2+2H_2O$, as shown by J. B. A. Dumas, and C. F. Anthon. H. L. F. Melsens found it to be an advantage to mix the acid and sulphur with pumice-stone. E. Hart recommended warming sulphur with fuming sulphuric acid, containing 30 per cent. SO_3, when the blue soln. so formed is heated, sulphur dioxide mixed with some trioxide is given off. The evolution of the dioxide ceases when all the trioxide has been acted upon, and the sulphur melts. J. Knezaurek obtained sulphur dioxide by heating sulphuric acid with charcoal: $2H_2SO_4+C=2H_2O+2SO_2+CO_2$, for purposes where the admixed carbon monoxide and dioxide will do no harm. W. L. Scott recommended using acid of sp. gr. 1·824 containing 74 per cent. SO_3. If a more conc. acid is used, a portion is reduced to sulphur; and if a more dil. acid is employed, some hydrogen sulphide is formed. The washing liquid should be mixed with lead sulphate or coarsely powdered charcoal. One of the commonest methods of preparing small quantities of sulphur dioxide is to heat conc. sulphuric acid with copper: $Cu+2H_2SO_4=SO_2+2H_2O+CuSO_4$—*vide* **3.** 21, 6. According to G. J. Warner, sulphuric acid is reduced to sulphur dioxide at 160°, and S. Cooke showed that the reaction is accelerated by the presence of platinum. C. Bollé heated nitre-cake, acid sodium sulphate with wood-shavings and coke; J. S. and A. A. Blowski, with petroleum sludge; G. Schildhaus and C. Condrea, with acid-tar or sludge; and I. P. Llewellyn and P. Spence, and P. Hart with pyrites in order to obtain sulphur dioxide. Sulphur dioxide is formed by the action of conc. mineral acids on sulphites, on thiosulphates, and on all polythionic acids. L. G. Wesson found that solid metahydrosulphite alone or mixed with a dry solid pyrosulphate is hygroscopic in moist air, and gives off sulphur dioxide. G. Neumann obtained sulphur dioxide from a Kipp's apparatus by using cubes made of calcium sulphite and plaster of Paris, and conc. sulphuric acid. E. Geisel, and F. W. Küster and F. Abegg devised an apparatus for preparing the gas from conc. sulphuric acid and soln. of hydrosulphites. W. Garroway decomposed a soln. of sodium hydrosulphite by sodium hydrosulphate or sulphuric acid. Most of the sulphur dioxide is driven out in the cold, the remainder by the injection of steam. L. Monnet fused a mixture of alkali hydrosulphite and sodium thiosulphate, and found sulphur dioxide is given off when the granulated mass comes in contact with water. P. Pierron obtained sulphur dioxide at the anode during the electrolysis of ammonium thiosulphate. F. Clausnizer observed that sulphur dioxide is formed by the action of phosphorus pentabromide on sulphuric acid; E. Divers and T. Haga, by the action of alkali metals on nitrosulphates; and H. Beckurts and R. Otto, by heating chlorosulphonic acid to 170°–180°. E. Cardoso discussed the preparation and purification of the gas.

According to A. Gautier, water vapour attacks sulphides of the heavy metals —FeS, PbS, etc.—at an incipient red-heat, forming hydrogen sulphide, hydrogen, and sulphur dioxide. In some cases, the sulphide is reduced to metal—*e.g.* $Cu_2S+2H_2O=2Cu+SO_2+2H_2$. The sulphur of hydrogen sulphide may be oxidized by the oxygen of water-vapour at a red-heat giving sulphur dioxide, hydrogen, and traces of sulphur, sulphuric acid, and thionic acids. Hence, the presence of oxygen is not necessary to account for sulphur dioxide in volcanic gases.

Sulphur dioxide for liquefaction is made by a process which gives a product of a higher degree of purity than is needed for some operations. If the sulphur dioxide is diluted with much inert gas, it requires concentration. This subject is discussed in a special monograph by A. Harpf, and E. Schütz. In some cases, the burner gases are scrubbed with water, cooled with water, and the resulting liquid heated in order to recover the absorbed sulphur dioxide—*e.g.* R. Pictet, F. R. Carpenter, H. Hegeler and N. L. Heinz, Compagnie Industrielle des Alcools de l'Ardèche, E. Schroeder and M. Haenisch, A. H. Eustis, etc. Other liquids have been recommended in place of water—*e.g.* E. Bergmann and T. Berliner used a soln. of calcium hydrophosphate ; F. E. Coombs, milk of lime or sodium carbonate ; H. K. Moore and R. B. Wolf, calcium chloride ; J. L. Babé and H. Pape, a soln. of an indifferent salt ; F. Kuhlmann, heavy coal-tar oil ; P. Pascal, carbolic oil ; etc. F. W. Andrews discussed the purification of commercial sulphur dioxide by fractional volatilization of the liquid.

The physical properties of sulphur dioxide.—At ordinary temp. and press., sulphur dioxide is a colourless gas of suffocating smell. It can be condensed to a colourless liquid, and frozen to a colourless, transparent, crystalline solid. The **relative density** of the gas, air unity, was found by H. Davy[4] to be 2·193 ; T. Thomson gave 2·2222 ; R. F. Marchand, 2·0412 ; H. V. Regnault, 2·221 ; J. Buff, 2·2277 ; J. J. Berzelius, 2·247 ; J. L. Gay Lussac, 2·255 ; L. Bleekrode, 2·234 at 15° ; A. Leduc, 2·2639±0·0001 ; G. Bauer, 2·881 at 716 mm., and 2·910 at 724 mm. D. Berthelot gave 2·04835 (oxygen unity) at 0° and 1 atm. press. E. Mathias found the density, D, of the sat. vapour of sulphur dioxide can be represented by $D=1·4328\{1-m-1·140(1-m)^{\frac{1}{2}}+0·579^2\}$, where m represents temp. referred to the critical temp. as unit, $m=T/T_c$; or $D=1·0019-0·00334\theta-0·07887(156-\theta)^{\frac{1}{2}}$. L. P. Cailletet and E. Mathias found the density of the sat. vapour of sulphur dioxide, referred to water at 4°, to be :

	7·3°	24·7°	58·2°	78·7°	100·6°	123·0°	144·0°	154·9°
Density .	0·00624	0·0112	0·0310	0·0464	0·0786	0·1340	0·2495	0·4017

Towards the critical temp. 156°, the density of liquid and gas approach the limiting value 0·52. C. von Linde gave 0·002861 for the density of the gas at 0°—water unity ; and G. Bauer, 0·00286 at —10° and atm. press. E. Exner made some observations on this subject. The **weight of a normal litre** of sulphur dioxide was found by A. Leduc to be 2·9267 grms. and for the weight W of gas at normal press. when the weight is W_p at a press., p, between 0·5 and 1·0 atm., is $W=W_p 760\{1+0·0000323(760-p)\}/p$, A. Jaquerod and A. Pintza found 2·92664±0·0001 grms. when the value for oxygen was 1·4292 grms. The weight of a litre of the gas at 0° was 2·18172 grms. at 570 mm. press., and 1·44572 grms. at 380 mm. press. G. Baume gave 2·9266 grms. for the weight of the normal litre, and the coeff. representing the deviation from Boyle's law is 0·02380 between 0 and 1 atm. press. M. S. Blanchard and S. F. Pickering reviewed the literature on this subject. M. Faraday gave 1·42 for the **specific gravity** of liquid sulphur dioxide ; A. Bussy, 1·45 ; L. Dufour, 1·49 at —20° ; J. I. Pierre, 1·4911 at

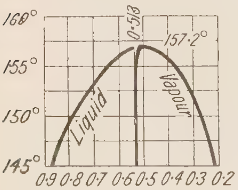


FIG. 44.—Law of Rectilinear Diameter for Liquid and Gaseous Sulphur Dioxide.

−20·5° ; E. d'Andréeff, 1·4333 at 0° ; L. Bleekrode, 1·359 at 15° ; R. Nasini, 1·3667 at 24° ; and L. P. Cailletet and E. Mathias :

	0·0°	21·7°	52·0°	102·4°	120·45°	140·8°	151·75°	155·05°
Sp. gr. .	1·4338	1·3757	1·2872	1·1041	1·0166	0·8690	0·7316	0·6370

E. Mathias said that the density between 90° and 146° can be represented by $1·2312(m-0·569+1·655\sqrt{1-m})$, where m denotes temp. referred to the critical temp. as unit. E. Cardoso found the law of the rectilinear diameter holds good except for a slight deviation near the critical point—Fig. 44. W. Herz discussed the sp. gr. of the liquid. A. Lange represented the sp. gr. D, and the mean coeff. of cubical expansion, β, of the liquid, by

	−50°	−40°	−30°	−20°	−10°	0°	10°	20°
D .	1·5572	1·5331	1·5090	1·4846	1·4601	1·4350	1·4095	1·3831
β .	—	0·00157	0·00160	0·00164	0·0016	0·00175	0·00182	0·00192

	30°	40°	50°	60°	70°	80°	90°	100°
D .	1·3556	1·3264	1·2957	1·2633	1·2289	1·1920	1·1524	1·1100
β .	0·00206	0·00223	0·00240	0·00261	0·00285	0·00315	0·00350	0·00390

The change of vol. δv with temp. was measured by J. I. Pierre, C. Drion, and E. d'Andréeff ; while A. Lange found :

	−30°	−20°	0°	20°	40°	60°	80°	100°
δv .	0·9510	0·9666	1·0000	1·0375	1·0819	1·1389	1·2039	1·2929

C. L. Berthollet[5] found the sp. gr. of a sat. aq. soln. of sulphur dioxide to be 1·040 ; T. Thomson, 1·0513 ; R. Bunsen and F. Schönfeld gave 1·06091 at 0° ; 1·05472 at 10° ; 1·02386 at 20° ; and 0·95548 at 40°. At 15°, A. Scott found for soln. with

SO_2 .	0·5	1·0	2·0	4·0	6·0	8·0	10·0 per cent.
Sp. gr.	1·0028	1·0056	1·0113	1·0221	1·0328	1·0426	1·0520

Observations were also made by E. F. Anthon, R. Wagner and L. Gautier, H. Schiff, G. T. Gerlach, H. Hager, C. Umney and T. Tyrer, and T. H. Sims. W. B. Giles and A. Shearer showed that a good approximation to the relation between the sp. gr., D, and the percentage composition of the soln., p, can be represented by $D=1+0·005p$, at 15·4°, and 760 mm. This means that the percentage of SO_2, multiplied by 5, gives the sp. gr. of the soln. over and above 1000. Thus, for instance, a soln. containing 1 per cent. of SO_2 has a sp. gr. of 1·005, one of 5 per cent. a sp. gr. of 1·025, one of 10 per cent. a sp. gr. of 1·050, and so on ; so that, on the other hand, if we know the sp. gr., we can at once tell the percentage of SO_2, provided that this is the only body present to influence the sp. gr. L. Carius represented the sp. gr. of a soln. of the gas in alcohol at 760 mm. and θ° by $1·11937-0·014091\theta+0·000257\theta^2$. The mol. vol. was studied by E. Rabinowitsch, who gave 44 for that constant. W. Herz studied this subject ; and J. J. Saslawsky and co-workers, the changes in vol. on neutralization with soda-lye.

The **compressibility** of the gas was measured by E. H. Amagat ;[6] he found that instead of the ratio pv/p_1v_1 being unity, in accord with Boyle's law, the values at different temp. were :

	15°	50°	100°	150°	200°	250°
pv/p_1v_1 .	1·0185	1·0110	1·0054	1·0032	1·0021	1·0016

D. I. Mendeléeff and W. Hemilian found that at press. exceeding one atm., there is a negative deviation from Boyle's law, meaning that the compressibility is greater than corresponds with that law, while for press. between 20 and 60 mm. there is a positive deviation from Boyle's law, meaning that the compressibility is smaller than required by that law. According to F. Fuchs, the value of pv increases as the press. falls from 1000 mm. to 250 mm., thus :

p .	1000	900	800	700	600	500	400	300	250 mm.
pv .	10000	10033·6	10067	10100	10133	10166·4	10198	10225	10251

D. Berthelot gave 0·025992 for the compressibility coeff. of the gas. If A denotes the deviation of the gas from Boyle's law $1-pv/p_1v_1=0$, such that $A=1-pv/p_1v_1$ —as indicated **1.** 6, 8—then A. Jaquerod and O. Scheuer found that below one atm. press., $A'_0=0·02314$; and E. Wourtzel, $A'_0=0·02379$; $A'_{0·5}=0·02386$; and $A'_{0·25}=0·02360$. L. P. Cailletet gave 0·0003014 for the compressibility of the liquid at —14° and 606 atm. press.; while A. Lange gave:

	15·4° (14·0)	16·3° (14·3)	18·6° (14·1)	68·8° (10·8)	92·1° (8·3)
Compressibility coeff. .	$0·0_3134$	$0·0_3132$	$0·0_3135$	$0·0_3271$	$0·0_3467$

where the bracketed terms refer to press. expressed in atm. F. Isambert gave 0·0001024 for the compressibility coeff. of a soln. of 60 litres of sulphur dioxide in a litre of alcohol at 18·9°; 0·0001041 at 19·1°; and 0·0001028 at 20·3°. D. Berthelot and P. Sacerdote measured the compressibility of mixtures of carbon and sulphur dioxides and the result is less than the value calculated by the additive rule. A. Leduc also found that when the two gases are mixed there is a slight increase in press. above that calculated from the law of partial press.

The **surface tension** of liquid sulphur dioxide was found by L. L. Grunmach[7] to be $\sigma=33·29$ dynes per cm., and the **specific cohesion,** $a^2=4·519$ sq. mm. F. W. Clark gave $\sigma=2·3$ mgrms. per sq. mm. at —15°. V. M. Stowe found the surface tension of liquid sulphur dioxide to be represented by $\sigma=0·061534(157·5-\theta)^{1·2}$, at temp. between —20° and 50°. Some observed results were:

	—20°	—10°	5°	15°	20°	30°	40°	50°
σ .	30·68	28·59	25·58	23·64	22·73	20·73	18·77	16·85

J. B. Hannay observed that the capillary attraction vanishes at the critical temp. and is not restored by increasing the press. C. A. Valson, in his study of capillarity as an additive property, found what he called the **capillary modulus** of the radicle SO_3'' at 15°, with a capillary tube 0·5 mm. in diameter to be 1·3. F. F. Fitzgerald found the **viscosity,** η, of liquid sulphur dioxide to be 0·003936 at 0°; 0·004285 at —10·5°; 0·004521 at —15°; and 0·005508 at —33·5°. J. Dubief made observations on the relation between the viscosity and density of the liquid. C. J. Smith obtained 0·0001168 for the viscosity of the gas at 0°; 0·0001253 at 18°; and 0·0001630 at 100°; and 416 for Sutherland's constant—**1.** 13, 3. T. Graham gave for the viscosity of the gas at 0°, 0·0001225, and at 20°, 0·0001380; and H. Vogel gave 0·0001183 at 0°. O. E. Meyer gave 0·000145 referred to air 0·000200; and O. E. Meyer and F. Springmühl, 0·000138 between 10° and 20° referred to air 0·000212. M. Trautz and W. Weizel found the viscosity changes from $0·0_31221$ at 14° to $0·0_32071$ at 199°, with constant temp. coeff. over this range. Sutherland's constant does not apply to this gas. The viscosity curve of mixtures of sulphur dioxide and hydrogen exhibits a maximum, which, as the temp. increases, flattens, and is displaced towards mixtures richer in sulphur dioxide. At 17°, a mixture containing approximately 70 molar per cent. of hydrogen has a maximum viscosity, whilst at 199° the maximum occurs with the mixture containing 50 molar per cent. of hydrogen. The increase of viscosity of mixtures on the addition of hydrogen is roughly proportional, up to the maximum, to the molar fraction of hydrogen. Observations on the viscosity of sulphur dioxide were also made by A. von Obermeyer, H. Vogel, and S. Pagliani and M. Batelli. J. R. Lewis measured the viscosity of soln. of sulphur dioxide in carbon tetrachloride, acetone, benzene, toluene, xylene, ether, heptane, carbon disulphide, and water. F. Schuster gave 2726 atm. for the **internal pressure.** M. Faraday[8] concluded that mercury cannot confine gases permanently; but H. B. Dixon showed that with sulphur dioxide and some other gases there is no diffusion through mercury. If the mercury be dirty, or moisture be present, a film might be formed between the glass and the mercury which permitted diffusion. J. Loschmidt found that the coeff. of **diffusion** of sulphur dioxide into hydrogen at 0° is 0·48278 sq. cm. per sec. K. Kanata studied the permeability of rubber for the gas. A. Masson, and G. Schweikert gave for the

velocity of sound in the gas, 209·0 metres per sec. at 0°. N. de Kolossowsky studied the relation between the velocity of sound and the speed of translatory motion of the molecules.

The **molecular weight** of sulphur dioxide calculated from the vap. density is 64·046 by D. Berthelot;[9] and 64·059±0·006 by E. Wourtzel. From the method of limiting densities, G. Baume calculated 64·039; and from the critical constants, 63·954. From the regularities in the b.p. of various liquids, H. M. Vernon assumed that the molecule is to be represented by SO_2. P. Walden and M. Centnerszwer found that the ebulliscopic constant of liquid sulphur dioxide agrees with the assumption that the molecule is SO_2; and W. Vaubel, that the molecule is $(SO_2)_{1\cdot78}$. P. A. Guye found that the mol. wt. at the critical temp. is in accord with the value calculated by vap. density law. O. E. Meyer calculated the **molecular diameter** of sulphur dioxide to be $1\cdot21\times10^{-7}$ cm.; E. Dorn, $0\cdot69\times10^{-7}$ cm.; and F. Exner, $1\cdot7\times10^{-8}$ cm. O. E. Meyer gave $\lambda=0\cdot0000047$ for the **mean free path** of the molecules; for the **collision frequency,** 639×10^6 per second; for the **velocity** of mean square 324 metres per second; and for the mean velocity 298 metres per second. C. J. Smith calculated $0\cdot94\times10^{-15}$ sq. cm. for the mean collision area, and A. O. Rankine and C. J. Smith found that this result agreed better with that deduced from the formula $S\lhd O_2$ than that from O=S=O. J. E. Mills made observations on the **intermolecular attraction.** W. Nernst gave 3·3 for the **chemical constant.** According to P. A. Guye and L. Friedrich, the **constants in J. D. van der Waals' equation—1**. 13, 4—are $a=0\cdot01345$ and $b=0\cdot00251$ referred to the initial vol. of the gas; $a=6\cdot61\times10^6$, and $b=55\cdot7$ referred to mols; and $a=1610$, and $b=0\cdot870$ referred to grams. D. Berthelot gave $a=0\cdot028544$, and $b=0\cdot005384$ referred to the initial vol. of the gas. J. Dubief studied the co-volume and equation of state; W. Herz, the co-volume; and M. F. Carroll, W. Herz, and K. Wohl, the equation of state. M. Trautz and O. Emert, M. Trautz and M. Gürsching, P. Sacerdote, A. Leduc, and F. Braun studied the application of the partial press. law to mixtures of sulphur dioxide with hydrogen, nitrogen, oxygen, air, ether, and carbon dioxide.

H. V. Regnault[10] gave 0·003903 for the coeff. of **thermal expansion** of sulphur dioxide at constant press. between 0° and 100°; G. W. Walker, 0·00390 at 0° and 760 mm.; A. Leduc, 0·00396 between 0° and 20° at normal press., and under a press. of 334 mm., 0·003787 between 0° and 22°; G. Magnus, 0·003856; and E. H. Amagat, at normal press.:

	0°–10°	10°–20°	50°	100°	150°	200°	250°
α .	0·004233	0·004005	0·003846	0·003757	0·003718	0·003695	0·003685

For dry sulphur dioxide at ordinary temp. he gave 0·00390, and for the moist gas, 0·00395–0·00396. A. Leduc gave for the coeff. of the increase of press. with temp., 0·003883 at 0°. H. V. Regnault gave 0·003845 at constant vol. C. Langer and V. Meyer showed that at about 1690°, the coeff. of expansion is nearly the same as that of nitrogen, and Charles' law of expansion is followed at this temp. The gas is not dissociated at 1700°. P. de Heen found that between 1° and 130°, $dv/d\theta=\alpha v^{2\cdot333}$, where α denotes the coeff. of thermal expansion at 0°. L. P. Cailletet and E. Mathias found for the coeff. of cubical expansion of the liquid between

	153°–154°	154°–155°	155°–155·5°	155·5°–156°
Coeff. expansion .	0·07721	0·1345	0·2273	0·7371

Observations were also made by V. N. Thatte, J. I. Pierre, C. Drion, and E. d'Andréeff. A. Lange's results are indicated in connection with the effect of temp. on the sp. gr. of the liquid. He found that at about 95°, the coeff. of expansion of the liquid is nearly the same as that of the gas; and C. Drion said that this occurs at about 100°. A. Eucken gave 0·01950 cal. per cm. per sec. per degree for the **thermal conductivity** of sulphur dioxide gas at 0°. S. Chapman and W. Hainsworth studied the thermal diffusion of mixtures of hydrogen and sulphur dioxide.

A. Masson[11] found the ratio of the two **specific heats** of sulphur dioxide to be 1·280 at 0°, and for the mol. ht., $C_p=9{\cdot}834$, and $C_v=7{\cdot}682$; H. V. Regnault gave for the sp. ht. at constant press., $c_p=0{\cdot}1544$, at 15°–200°, or $C_p=9{\cdot}891$; A. Cazin gave for the ratio of the two sp. hts., 1·262, at 20°; and P. A. Müller, 2·2563 at 20°. R. Thibaut found for the ratio of the two sp. hts., at 20°, 1·258 at one atm. press., and 1·273 at $\frac{1}{3}$ atm. press; K. Schöler gave 1·273 at 0·5 atm. press., 1·283 at 1 atm., and 1·323 at 2 atm. press., and 20°; B. Berneis gave $C_p=9{\cdot}1490$ at 20°–100°, or $C_p=9{\cdot}00+0{\cdot}0074\theta$; M. Trautz and B. Berneis, $C_p=9{\cdot}00+0{\cdot}0037\theta$. J. R. Partington and H. J. Cant gave for the ratio of the two sp. ht., 1·291, and $C_p=9{\cdot}476$ and $C_v=7{\cdot}340$; and G. Schweikert, 1·266 at 0°, G. N. Lewis and M. Randall gave $C_v=7{\cdot}0+0{\cdot}0071\theta+0{\cdot}05186\theta^2$; R. Furstenau, $C_p=9{\cdot}18+0{\cdot}003077\theta$; and B. Berneis, $C_p=9{\cdot}00+0{\cdot}0074\theta$. B. Neumann calculated the following values for the sp. ht.:

	0°	100°	200°	400°	600°	800°	1000°	1100°	1500°	2000°	2400°	2600°	2800°	3000°
Sp. ht.	0·139	0·148	0·158	0·177	0·190	0·199	0·204	0·206	0·2125	0·219	0·223	0·226	0·230	0·231

G. Witz made some observations on the heat of capacity of the gas. E. Mathias gave for the sp. ht. of the liquid between −20° and 155·5°, $c=0{\cdot}3172+0{\cdot}0003507\theta-0{\cdot}000006762\theta^2$; and A. Nadeschdine gave 0·3178 for the sp. ht. between −20·6° and 9·8°. A. Press studied some relations of the sp. ht. P. Duhem showed that if the sp. ht. of a saturated vapour is plotted against temp., the form of the curve is that of an inverted, unsymmetrical U; and that sometimes this lies wholly in the negative region, but in other cases it may cross into the positive region, but if it does so it crosses twice. E. Mathias gave for the sp. ht. of the sat. vapour, c_v, and for the sp. ht. of the sat. liquid, c_l, of sulphur dioxide:

	−20°	0°	40°	90°	100°	110°	120°	140°	155°
c_v .	—	−0·410	−0·300	−0·095	+0·027	+0·062	−0·078	−0·620	−3·850
c_l .	0·315	0·317	0·338	0·403	0·422	0·442	0·470	0·620	1·800

The sp. ht. of the sat. liquid is not a linear function of the temp. even when remote from the critical temp. The subject was discussed by J. A. Ewing, W. Jazyno, and A. W. Porter. U. Bordoni studied the entropy of the system H_2O–SO_2.

A. F. de Fourcroy[12] has stated that G. Monge and L. Clouet discovered that sulphur dioxide can be liquefied by 28° of cold, and he added that "this property distinguishes sulphur dioxide from all other gases, and it appears to be owing to the water which it holds in solution, and to which it adheres so strongly as to prevent an accurate estimate of the proportion of its radicle and acidifying principles." Notwithstanding A. F. de Fourcroy's objection, M. Faraday said that "there can be little doubt that G. Monge and L. Clouet did actually condense the gas, for he found that the small elastic force of its vapour at common temp. is only about 2 atm., so that a comparatively moderate diminution of temp. is sufficient to retain it liquid at common press., or a moderate additional press. to retain it liquid at common temp." M. Faraday obtained the liquid by pumping the dried gas, at 3 to 5 atm. press., into an evacuated and cooled tube; A. Bussy cooled the dried gas with a mixture of ice and salt; G. F. Wach, and F. Wöhler placed sulphur and sulphuric acid in one leg of a bent sealed tube, and gently warmed the mixture; the other leg of the tube was cooled by ice and salt; H. L. F. Melsens, and A. Verneuil used charcoal sat. with sulphur dioxide as the source of the gas in the sealed tube; and A. Loir and C. Drion cooled the gas by evaporating ether. A. W. Hofmann said that glass tubes are dangerous in experiments on the liquefaction of the gas, and B. Krecsey recommended copper vessels. The liquefaction of the gas industrially was discussed by E. Schröder and M. Hänisch, A. Lange, H. J. Paoli, and A. Harpf. The liquid dioxide is sold for laboratory purposes in glass syphons, fitted with a screw-valve, so arranged that either liquid or gas can be drained off. A. Bussy observed that if liquid dioxide be rapidly evaporated under an evacuated bell-jar, a part of the liquid forms white flecks; and J. K. Mitchell obtained the solid by surrounding the liquid with a mixture of solid carbon dioxide and ether. J. K. Mitchell gave —79° for the **melting point** of the solid; M. Faraday, —76·1°; A. Smits and W. J. de Mooy, —75·6°; T. P. van der Goot, —75·1°; W. F. Seyler and A. F. Gill, —72·8°; P. Walden and M. Centnerszwer, —72·70°; and G. Baume and A. Tykociner, —72·5°. For the **boiling point** at ordinary press., M. Faraday, E. d'Andréeff, and L. Dufour gave —10°; J. M. Pierre and C. Drion, —8° at 759·2 mm.; H. V. Regnault, —10·08° at 760 mm.; R. Bunsen, —10·5° at 744 mm.; A. Nadeschdine, —10° at 757 mm. press.; F. W. Bergstrom, —10·02°; T. Estreicher, —10·1°; J. Henning and A. Stock, —9·99° at 760 mm.; G. A. Burrell and I. W. Robertson, —11·0° at 760 mm.; and H. D. Gibbs, —10·09 at 760 mm. N. de Kolossowsky gave 1·43 to 1·60 for the **ebulliscopic constant** of the liquid. M. Faraday measured the **vapour pressure** of liquid sulphur dioxide between —10° and 37·77°; H. V. Regnault, between —30° and 65°; W. Sajontschewsky, between 50° and 155·4°; R. Pictet, between —30° and 50°; W. Mund, between —42° and 0°; A. Blümcke, between —19·5° and 98·2°; G. A. Burrell and I. W. Robertson, between —11° and —64·5°; F. Henning and A. Stock, between 10° and —181°; F. W. Bergstrom, between —5·5° and —90·1°; W. Mund, between —42° and 0°; and E. Briner and E. Cardoso, between 33·5° and 72·2. Observations have also been reported by E. Cardoso and U. Florentino, O. Scheuer, A. Stock, A. Rex, B. Leinweber, B. D. Steele and L. S. Bagster, A. Stock and co-workers, E. Cardoso and co-workers, and P. M. Shen. The following is a composite summary of the results:

	Solid.			Liquid.					
	−90·1°	−81·3°	−72·9°	−61·71°	−51·18°	−36·13°	−25°	−10°	−9·99°
p mm. .	2·5	7	16	38·2	80·2	199·95	373·79	762·49	760

and for the liquid above 0°:

	0°	20°	33·5°	50°	77·5°	80°	100°	120°	150°
p atm. .	1·52	3·27	4·80	8·31	17·12	18·09	27·82	41·56	71·45

C. E. and O. Maass gave for the vap. press., *p* cm.:

	0·2°	1·3°	2·25°	10·0°	16·5°	22·0°	27·0°
p .	117·27	123·5	127·6	173·3	218·8	264·1	314·2

H. V. Regnault represented his results by the equation $\log p=5{\cdot}6663791-3{\cdot}01468920\alpha^{\theta+28}-0{\cdot}1465400\beta^{\theta+28}$, where $\log \alpha=9{\cdot}9972989-10$; and $\log \beta=9{\cdot}98729002-10$. C. Antoine used $\log p=0{\cdot}98215\{7{\cdot}3593-1000(\theta+236)\}$. G. A. Burrell and I. W. Robertson gave $\log p=-1448{\cdot}01T^{-1}+8{\cdot}425$ for the liquid between —11° and —64·5°; and for the solid between —90·6° and —144·1°, $\log p=-1232{\cdot}2T^{-1}+9{\cdot}579$; F. W. Bergstrom gave for the liquid $\log p=1577{\cdot}3T^{-1}+1{\cdot}75\log T-0{\cdot}006411T+6{\cdot}3286$; and F. Henning and co-workers, $\log p=-1561{\cdot}36T^{-1}+1{\cdot}75\log p=0{\cdot}0061757T+6{\cdot}20476$. V. Kirejeff discussed what he called the cohesion press. of sulphur dioxide. According to F. Braun, the press. of the saturated vapour at the b.p. is 3·9 mm. less in an atm. of carbon dioxide, and 1·3 mm. less in an atm. of nitrogen than it is in vacuo. Liquid sulphur dioxide for ice machines was employed by R. Pictet. He used at first a mixture of approximately equimolar parts of carbon and sulphur dioxides, and later a mixture of 32 molar parts of sulphur dioxide to one molar part of carbon dioxide—the so-called *Pictet's liquid.* The vap. press., *p* atm., of a mixture of sulphur dioxide with 0·4 per cent. of carbon dioxide was found by A. Rilliet to be:

	−22·5°	−17°	−9°	−4·5°	2·4°	15·5°	20°	36°
p .	0·97	1·19	1·48	1·71	2·10	3·21	3·68	6·0

while H. V. Regnault gave for the liquids separately

		−20°	−15°	−10°	0°	10°	20°	30°	40°
p	SO_2 .	0·63	0·80	1·00	1·53	2·26	3·24	4·52	5·28
	CO_2 .	19·93	23·14	26·76	35·40	46·05	58·84	73·84	82·17

Hence, added R. von Schöttler, Pictet's liquid has the advantage over sulphur dioxide that its vap. press. within ordinary limits of temp. does not fall below atm. press., and is not nearly so high as carbon dioxide. This subject was also examined by A. Blümcke. In place of Pictet's liquid, C. M. Tessié du Motay employed a soln. of sulphur dioxide in ether; J. Quiri, a soln. of the gas in hydrocarbons—*iso*butylene, propylene, butane, or pentane; and P. Boessneck, a soln. in acetone. T. K. Sherwood measured the partial press. of sulphur dioxide over its aq. soln.—*vide infra*, the effect of press. on the solubility of the gas in water. F. Caubet studied the *pv*-relation with binary mixtures of sulphur dioxide and carbon dioxide, and methyl chloride—**1**. 4, 3; E. Briner and E. Cardoso, with mixtures of sulphur dioxide and methyl ether; and W. Mund and P. Herrent, sulphur dioxide and ethane.

C. Drion gave 140° for the **critical temperature** of sulphur dioxide; A. Ladenburg, 157°–161°; W. Sajotschewsky, 155·4°; P. Hein, 157·24°; K. Schuck, 155·1°; M. Centnerszwer, 157·26°±0·2°; P. Niggli, 157·6°; M. W. Travers and F. L. Usher, 157·3°; J. Dewar, and P. A. Guye, 154·4°; L. P. Cailletet and E. Mathias, 156·0°; E. Cardoso and R. Bell, 157·15°±0·10°; and E. Briner, 157·2°. The subject was studied by W. Herz, and E. Cardoso. E. Cardoso and R. Bell said that the point of opalescence could not be observed at the critical temp. owing to an opalescent deposit on the glass. This is supposed to be produced by the action of light and heat on the gas, although heating the gas for 300 hrs. did not affect the critical constants. L. P. Cailletet and E. Mathias said that the presence of a trace of air lowers the observed critical temp.; and M. Centnerszwer found that the mol. lowering of the critical temp. is independent of the nature of the substance present, and for a mol in 100 c.c. of liquid sulphur dioxide, amounts to 724°. P. A. Guye, W. Sajontschewsky, and J. Dewar gave 78·9 atm. for the **critical pressure**; E. Cardoso and R. Bell, 77·65±0·10 atm.; E. Cardoso and co-workers, 77·79; and E. Briner, 77·95 atm. P. A. Guye gave 2·2 for the **critical density** with respect to air at 0° and 760 mm.; E. Cardoso and E. Sorrentino, 0·5240±0·0005; and L. P. Cailletet and E. Mathias gave 0·520 at 156° with respect to water at 4°, and E. Cardoso and R. Bell, 0·513; and for the **critical volume** 0·00557, L. P. Cailletet and E. Mathias gave 0·00550–0·00587; and F. Schuster, 0·00538. W. Herz studied the relations of the critical constants. S. F. Pickering gave for the best representative values, T_c=430·3° K.; P_c=77·7 atm.; and D_c=0·52. W. Herz studied the critical constants of sulphur dioxide. J. Chappius found the **heat of vaporization** of liquid sulphur dioxide to be 91·7 cals. per gram, or 5·88 Cals. per mol. T. Estreicher found 96·2 cals. per gram or 6·16 Cals. per mol; at the b.p., −10·1°; T. Estreicher and A. A. Schnerr, 95·3 cals. per gram or 6·11 Cals. per mol at the b.p. −11·16°; G. A. Burrell and I. W. Robertson gave 6·196 Cals. per mol. The values calculated by L. P. Cailletet and E. Mathias are:

	0°	10°	20°	30°	40°	50°	60°
Heat of vaporization	91·2	88·7	84·7	80·5	75·5	70·9	69·0 cals.

H. Crompton calculated values in agreement with these results. E. Mathias gave for the latent heat, L, at θ, $L=91·87-0·3842\theta-0·000340\theta^2$, and between 0° and 50°, $L=91·87-0·3842\theta$. If λ denotes the internal latent heat of vaporization at θ°, and Q the quantity of heat necessary to raise the temp. of a gram of sat. vapour from 20° to θ°:

θ .	155·8°	151·85°	144·08°	128·00°	121·00°	102·65°	20·00°
λ .	−41·72	−37·70	−33·52	−31·17	−32·82	−29·20	0 cals.
Q .	4·75	12·67	20·49	27·72	27·72	35·51	35·51 cals.

G. Cantoni made some measurements of the heat of vaporization; N. de Kolossowsky studied the relation between the thermal expansion and the heat of vaporization; and P. H. Boutigny illustrated the latent heat of evaporation of sulphur dioxide by the freezing of water in a red-hot crucible:

> A little water was introduced into a platinum crucible heated to redness. The liquid assumed the spheroidal state. Some liquid sulphur dioxide was introduced by means of a pipette. The liquid evaporated very rapidly, and on simultaneously inverting the crucible a small mass of ice appeared.

F. B. Kenrick and co-workers found that liquid sulphur dioxide could be superheated to 50° for 5 seconds without explosion. W. Mund and P. Herrent investigated the liquefaction of mixtures of ethane and sulphur dioxide. According to P. A. Favre, it requires 0·261 Cal. to produce one c.c. of vapour from liquid sulphur dioxide; the heat of liquefaction for a mol of sulphur dioxide is 11·288 Cals., and for the heat of condensation when the gas is adsorbed by wood charcoal, 10·734 Cals.

P. L. Dulong [13] found the **heat of formation** of sulphur dioxide gas from solid sulphur to be $(\alpha\text{-S},\text{O}_2)=83\cdot2$ Cals.; H. Hess gave 82·2 Cals.; T. Andrews, 73·8 Cals.; P. A. Favre and J. T. Silbermann, 71·04 to 71·2 Cals.; M. Berthelot, 69·1 Cals.; J. Thomsen, 71·08 Cals.; J. R. Eckman and F. P. Rossini, 70·94 Cals.; and E. Petersen, 71·08 Cals. J. Thomsen, and E. Petersen gave for $(\beta\text{-S},\text{O}_2)$, 71·72 Cals.; M. Berthelot gave for colloidal sulphur, 69·1 Cals., and E. Petersen, 71·99 Cals., while for sulphur vapour, M. Berthelot gave 80·2 Cals. J. B. Ferguson obtained for the thermal value of the reaction with rhombic sulphur $\text{S}+\text{O}_2=\text{SO}_2$, $-68391+3\cdot62T\log T-0\cdot0007T^2+0\cdot0_631T^3-25\cdot04T$, or at 25°, −69,761 cals. For the **heat of solution** in water, J. Thomsen gave for a mol of the gas in 250 mols of water, 7·69 Cals.; for a mol of the liquid in 300 mols of water, 1·50 Cals.; $(\text{S},\text{O}_2,\text{Aq.})=78\cdot77$ Cals.; $(\text{SO}_{2\text{liquid}},\text{H}_2,\text{O},\text{Aq.})=76\cdot055$ Cals. P. A. Favre gave $(\text{SO}_{2\text{gas}},\text{Aq.})=7\cdot706$ Cals.; and M. Berthelot gave 8·34 Cals. for a mol of the gas in 5 litres of water, at 15°. P. Chappuis said that the heats developed by the soln. of the gas in water amounts to 0·000265 to 0·000359 Cal. per c.c. The **heat of adsorption** of the gas by wood charcoal was found P. Chappuis to be 0·000470 to 0·000615 Cal. per c.c. of gas, and P. A. Favre, 0·168 Cal. per gram of gas. A. G. Stiles and W. A. Felsing found the heat of soln. of a mol of sulphur dioxide with n mols of water is given by $Q=4911\cdot6+1105\cdot26\log_{10}n$(cals.).

E. Mascart [14] measured the **index of refraction** of sulphur dioxide gas, and P. L. Dulong gave 1·0006620 –air=1·0002923. L. Bleekrode found it to be 1·000686 for sodium light at 15°. E. Ketteler gave 1·0006907 for light of wave-length $535\mu\mu$; 1·0006860 for $\lambda=588\cdot9\mu\mu$; and 1·0006815 for $\lambda=670\cdot7\mu\mu$. L. Stuckert gave 696·3 for $\lambda=435\cdot9\mu\mu$; 1·0006666 for $\lambda=546\cdot1\mu\mu$; and 1·0006606 for $\lambda=670\cdot7\mu\mu$; G. W. Walker gave 1·000676 for $\lambda=589\cdot3\mu\mu$; and C. and M. Cuthbertson, 1·0006586 for $\lambda=500\mu\mu$; 1·000664 for $\lambda=546\cdot1\mu\mu$; 1·0006613 for $\lambda=580\mu\mu$; 1·0005671 for $\lambda=650\mu\mu$; and 1·0006564 for $\lambda=670\mu\mu$; and $\nu-1=5\cdot728\times10^{27}(8929\times10^{27}-\lambda^2)^{-1}$. J. Tauss and G. Hornung gave $1\cdot0_366618$ for $\lambda=656\cdot4\mu\mu$; $1\cdot0_367015$ for $\lambda=587\cdot6\mu\mu$; $1\cdot0_367658$ for $\lambda=546\cdot1\mu\mu$; and $1\cdot0_3689\cdot78$ for $\lambda=435\cdot8\mu\mu$. E. W. Cheney gave $1\cdot0_36637$ for $\lambda=5852$ A.; $1\cdot0_36615$ for $\lambda=6143$ A.; and $1\cdot0_36598$ for $\lambda=6678$ A. C. and M. Cuthbertson found that the refractivity is 18 per cent. less than that calculated by the law of mixtures. The dispersion electrons in sulphur dioxide appear to be equal to the sum of the dispersion electrons of sulphur and oxygen. M. Faraday said that the refraction of liquid sulphur dioxide is nearly the same as for water; but A. Delaire found it to to be rather greater. L. Bleekrode gave 1·350 at 15° for the *D*-ray, and 1·357 at 13° for sunlight; J. Dechant gave 1·340 at 20° for Na-light; and E. Ketteler, at 24·1°, 1·33574 for Li-light; 1·33835 for Na-light; and 1·34108 for Tl-light. W. Herz, and J. Tausz and G. Hornung studied the refraction of light with sulphur dioxide. L. Bleekrode obtained for the **refractive power** of the gas at 15° with the μ-formula, 0·236, and with the μ^2-formula, 0·157; while R. Nasini gave respectively 0·23937, and 0·14828; and for the liquid, L. Bleekrode obtained respectively 0·252 and 0·153 at 15° for Na-light. R. Nasini obtained respectively 15·32 and 9·49 for the **molecular refraction** of the gas. P. A. Guye observed a relation between the mol. wt. and the refractive index of substances in the vicinity of the critical temp. I. R. Rao discussed the scattering of light by sulphur dioxide.

G. D. Liveing and J. Dewar [15] found that the **ultra-violet absorption spectrum** of sulphur dioxide gas has a strong absorption band between the wave-lengths 3179 and 2630, and a feeble one between 3440 and 2300. M. le Blanc and co-workers found that sulphur dioxide has a maximum in the absorption spectrum at 2900, and a minimum at 2400. V. Henri, H. Deslandres, J. C. Ghosh and S. C. Bisvas, W. A Miller, L. Soret, F. Lowater, L. Ciechomsky, and W. H. Bair also examined the absorption spectrum of this gas. R. Wright found that while the aq. soln. of sulphur dioxide, or the crystal hydrates shows a selective absorption in the neighbourhood of the band $276\mu\mu$, the sulphites exhibit only a general absorption. This is taken to mean that in aq. soln. sulphurous acid consists largely of uncombined sulphur dioxide molecules. C. S. Garrett measured the molecular extinction with aq. soln. of sulphurous acid and of rubidium, potassium, sodium, and ammonium hydrosulphites of a concentration $C=0{\cdot}06[SO_2]/2$. The mol. extinction is defined by the ratio k/C, where $k=(I/d)\log(I_0/I)-d$, denoting the depth of the cell; I_0, the initial intensity of the light, and I, the emergent intensity. The results, with soln. 35 days old, are illustrated by Fig. 45. The curve for the alkali salts shows an increasing absorption with time; and it is inferred that at the moment of forming the soln., there would be no selective absorption. There is therefore a change in the soln. on keeping. This change is very greatly facilitated by light. The reaction in soln. is not hydrolytic: $NaHSO_3+H_2O=H_2SO_3+NaOH$ because the soln. are all acid to litmus; and the greatest change should occur with the ammonium salt, and be least with the rubidium salt. It is assumed that in light, the hydrosulphite is resolved into the normal sulphite and acid: $2NaHSO_3 \rightleftharpoons Na_2SO_3+H_2SO_3$; and that in soln., the sulphurous acid is resolved: $H_2SO_{3aq.}=SO_2.nH_2O$. The normal alkali sulphites show no selective absorption even when kept for a long time in light. Similar remarks apply to the mixed alkali, and alkali-silver sulphites; sodium acetonehydrosulphite; and the symmetrical and unsymmetrical diethyl sulphites. The alkali metadisulphites give the same selective absorption as do the hydrosulphites, and it is assumed that they are resolved by water: $Na_2S_2O_5+H_2O \rightleftharpoons 2NaHSO_3$. The absorption band given by the aged aq. soln. of sulphur dioxide is in the same position as the band given by the gas though somewhat broader. The absorption law is not followed since the band becomes shallower with increasing dilution. K. Schaeffer showed that the absorbing substance in aq. soln. is a hydrate $SO_2 \ldots H_2O$, which is more active than sulphur dioxide alone. The normal sulphites, and the alkyl sulphites are transparent in aq. soln., showing that sulphurous acid itself is probably non-absorptive, both ionized, and non-ionized. The decrease in the absorptive power on dilution is attributed to a change in the equilibrium $SO_2 \ldots H_2O \rightleftharpoons H_2SO_3$ from left to right. The aq. soln. contains very little sulphurous acid, and it is considered that measurements of the ionic conc. in sulphur dioxide soln. have given rise to false ideas regarding the degree of ionization of sulphurous acid, and consequently of the strength of the acid. At higher temp., soln. of sulphur dioxide absorb more strongly, owing to a shift in the equilibrium of the above equation towards the left. Similarly, the addition of sulphuric acid to an aq. soln. of the gas increases the depth of the band in the same manner, but only to a certain limit. When the sulphuric acid exceeds 5N, the absorption again decreases, probably owing to dehydration, in the sense $SO_2 \ldots OH_2 \rightarrow SO_2+H_2O$, the free sulphur dioxide being a less strong absorber than its hydrate. In pentane and chloroform soln. the absorption is similar to that of the free gas, and the soln. follow the absorption law. In soln. of methyl and ethyl alcohols and ethyl ether, the absorption is much increased, and in the case of ethyl ether the band passes into general

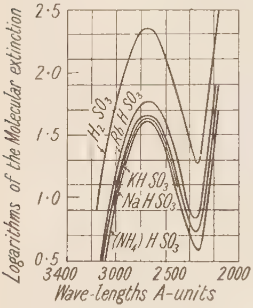


FIG. 45. — Absorption Spectra of Solutions of Sulphurous Acid and of Hydrosulphites.

absorption in the ultra-violet. These soln. also follow absorption law, and it is concluded that stable compounds of the type O_2S . . . OHEt and O_2S . . . OEt_2 must be present in such soln. Normal sulphites show only end absorption in the extreme ultra-violet, and when a soln. of a normal sulphite soln. is half neutralized with sulphuric acid, the resulting metal hydrogen sulphite soln. at first shows only end absorption, but after a few days, particularly under the influence of light, the sulphur dioxide band develops. When the metal hydrogen sulphite is formed, however, by mixing soln. of sulphur dioxide and normal sulphite, the band is present immediately. K. Schaeffer represents the equilibrium conditions in aq. soln. of sulphur dioxide by the schemes :

$$SO_2 \ldots H_2O \rightleftharpoons \begin{bmatrix} \mathrm{O} & & \mathrm{OH} \\ & \mathrm{S} & \\ \mathrm{O} & & \mathrm{H} \end{bmatrix} \rightleftharpoons \begin{bmatrix} \mathrm{O} & & \mathrm{O} \\ & \mathrm{S} & \\ \mathrm{O} & & \mathrm{H} \end{bmatrix} \mathrm{H} \rightleftharpoons \begin{bmatrix} \mathrm{O} & & \mathrm{O} \\ & \mathrm{S} & \\ \mathrm{O} & & \mathrm{H} \end{bmatrix}' + \mathrm{H}^{\cdot}$$

and

$$\begin{bmatrix} \mathrm{O} & & \mathrm{O} \\ & \mathrm{S} & \\ \mathrm{O} & & \mathrm{H} \end{bmatrix}' \rightleftharpoons \begin{bmatrix} & \mathrm{O} \\ \mathrm{OS} & \\ & \mathrm{OH} \end{bmatrix}' \rightleftharpoons \begin{bmatrix} & \mathrm{O} \\ \mathrm{OS} & \\ & \mathrm{O} \end{bmatrix}' \mathrm{H} \rightleftharpoons \begin{bmatrix} & & \mathrm{O} \\ \mathrm{O} & \mathrm{S} & \\ & & \mathrm{O} \end{bmatrix}'' + \mathrm{H}^{\cdot}$$

The hydrogen sulphite ion, HSO_3', is probably unstable and undergoes transformation into sulphurous acid and SO_3'', thus : $2HSO_3' = SO_3'' + H_2SO_3$. The sulphurous acid then comes into equilibrium with sulphur dioxide hydrate in the sense $H_2SO_3 \rightleftharpoons SO_2$ . . . H_2O. These changes explain the gradual development of the absorption band in hydrogen sulphite soln. The sulphite ion, $[SO_3]''$, probably has a symmetrical constitution, and hence also the normal sulphites. F. H. Getman also attributed the band at $276\mu\mu$ to hydrated sulphur dioxide formed from the ions of sulphurous acid : $H^{\cdot} + HSO_3' \rightleftharpoons H_2SO_3 \rightleftharpoons SO_2.H_2O$. Freshly prepared soln. of potassium metapyrosulphite, $K_2S_2O_5$, give a characteristic band at $263\mu\mu$ which disappears when the soln. has stood for some time and the $276\mu\mu$ band appears in its place. This is taken to mean that the $263\mu\mu$ band is due to the undecomposed salt. Soln. of sodium sulphite do not show selective absorption. Soln. of sodium hydrosulphite in light, and exposed to oxygen, develop the $276\mu\mu$ band, and some oxidation occurs. Light is said to be an essential factor in the oxidation. E. C. C. Baly's relation for the fundamental frequency in the ultra-red is applicable to the $263\mu\mu$ and the $276\mu\mu$ bands. According to E. C. C. Baly and R. A. Bailey, in aq. soln. of the hydrosulphites, there is present a small proportion of metahydrosulphite which absorbs light of wave-length $257\mu\mu$. In the absence of oxygen, these soln. are stable in light, but if oxygen is present photo-oxidation of the HSO_3'-ion takes place, followed by an ionic rearrangement whereby normal sulphate, sulphurous acid, and hydrated sulphur dioxide are produced. The soln. then shows the absorption band at $\lambda = 276\mu\mu$ characteristic of the hydrated sulphur dioxide. No isomerism of sulphite molecules has been detected. The absorption bands of sulphurous acid, hydrosulphite, and sulphite molecules lie in the extreme ultra-violet. The characteristic ultra-violet frequencies of sulphur dioxide, hydrated sulphur dioxide, and potassium metahydrosulphite are integral multiples of the fundamental molecular frequency of sulphur dioxide in the infra-red. R. Dietzel and S. Galanos say that the absorption spectra show that aq. soln. of sulphur dioxide contain chiefly unchanged mols. of sulphur dioxide and its hydrate, and only a small proportion of sulphurous acid and its ions.

Similarly with aq. soln. of alkali hydrosulphites. The greater absorption with alcoholic soln. is attributed to the formation of a complex $HO.SO.OC_2H_5$. The alteration which occurs when aq. soln. of the dioxide are exposed to light or warmed is attributed to a photo-oxidation of the HSO_3-ions which results in the formation of the normal sulphate, sulphurous acid, and the hydrate of sulphur dioxide. K. Schaeffer's assumption of an isomerization of the HSO_3-ions to explain this phenomenon is unnecessary. The wave-lengths of the bands in the ultra-violet spectrum of sulphur dioxide given by C. S. Garrett, and F. Lowater were shown by

J. Tyndall, E. C. C. Baly and C. S. Garrett to be related to the **ultra-red absorption spectrum** of sulphur dioxide observed by W. W. Coblentz. C. F. Meyer and co-workers, and V. I. Sihvonen studied the ultra-red spectra of the sulphites. In comparing the ultra-red spectrum of sulphur dioxide with that of carbon dioxide, the region where the latter is transparent, is where the former has its greatest absorption bands. The maxima of the absorption bands occur in $3{\cdot}18\mu$, $3{\cdot}97\mu$, $5{\cdot}68\mu$, $7{\cdot}4\mu$, $8{\cdot}7\mu$, and $10{\cdot}77\mu$. A. Balandin discussed the relation between the chemical affinity of sulphur dioxide, etc., and the ultra-red spectrum.

R. H. Sherry[16] studied the optical rotatory power of soln. of alkaloids in liquid sulphur dioxide. A. Kundt and W. C. Röntgen found that sulphur dioxide gas, at 150° and 20 atm. press., exhibits **electromagnetic rotation** of the plane of polarized light; and J. Kerr, that there is a feeble negative **electro-optical effect** with aq. soln. of sulphur dioxide. C. V. Raman and N. S. Krishnan, and G. Szivessy said that Kerr's constant is $-1{\cdot}67\times10^{-10}$ at 17·3°, and that it varies proportionally with the press. of the gas, and inversely as the wave-length of light. The subject was studied by H. A. Stuart. R. Dantinne and P. Lenaerts studied the photo-ionization of the gas in ultra-violet light; and L. Simons, the ionization of the gas by corpuscular rays.

According to A. S. Eve, the ionization produced by **X-rays** with sulphur dioxide is 2·3 (air unity); and R. K. McClung obtained for hard X-rays 4·79, and for soft X-rays, 11·05. E. Rutherford measured the velocity and rate of recombination of the ions of sulphur dioxide exposed to the X-rays; and P. W. Burbridge measured the absorption of the K-series of X-rays by sulphur dioxide. O. Stelling studied the absorption spectrum of the X-rays. P. W. Burbridge found that with mixtures of sulphur dioxide and air or carbon dioxide the X-ray absorption is additive. P. Lenard found that the absorptive power of sulphur dioxide for **cathode rays** at 760 mm. press. is 8·51 per cm. M. Ishino and B. Arakatsu found that in a positive ray tube the sulphur dioxide decomposes, forming negatively charged sulphur atoms. K. T. Compton gave 5·35 to 7·69 volts for the **ionizing potential.** S. C. Biswas studied the relation between the ionizing potential and the mol. vol.; L. B. Loeb, L. B. Loeb and L. du Sault, and H. R. Hasse, the mobilities of ions in the gas; A. Kirmann, the electrical moment of the molecules; W. A. Macky, the effect of sulphur dioxide on frictional electricity.

L. Bleekrode,[17] and A. Bartoli found that the **electrical conductivity** of gaseous sulphur dioxide above its critical temp. is zero, and that of the liquid in the vicinity of the critical temp. is very small. A similar result for the liquid was obtained by A. Delarive, and G. Magnus; while P. Walden and M. Centnerszwer found the conductivity of the liquid to be $0{\cdot}9\times10^{-7}$ at 0°; and P. Dutoit and E. Gyr gave $0{\cdot}85\times10^{-7}$ at $-15°$. K. T. Kemp must have worked with the moist liquid since he found that the liquid conducted as well as a metal and gave off oxygen at the anode, and sulphur at the cathode. J. Carvallo found that with liquid sulphur dioxide, free from air, with a difference of potential, E, between platinum electrodes, the current, C, diminishes with time until a limit is attained. The negative electrode becomes slightly brown, and the liquid is purified by the passage of the current. When $E=200$ to 500 volts, the limiting current does not vary as a simple function of E. When E is 1000–2000 volts, the current is smaller than that passing at a lower voltage. The $C=f(E)$ curves are in accord with Ohm's law when E does not exceed 100 volts. The limiting conductivity for higher voltages is not in agreement with this; the law governing it under these conditions resembles the laws for the conductivity of gases. The limiting sp. resistance under 100 volts was $7{\cdot}6\times10^{9}$ ohms; under 2350 volts, $4{\cdot}9\times10^{10}$ ohms, and under 4000 volts, $4{\cdot}9\times10^{10}$ ohms per cm. The conductivity of various substances dissolved in liquid sulphur dioxide has been measured by P. Dutoit and E. Gyr, L. S. Bagster and co-workers, M. Centnerszwer and J. Drucker, P. Walden and M. Centnerszwer, and E. C. Franklin. W. Ostwald, and P. Walden and M. Centnerszwer, and K. Barth have measured the mol. conductivity of soln. of sulphurous acid containing a mol of H_2SO_3 in v litres, and K. Barth found at 25°:

v .	32	64	128	256	512	1024	∞
μ .	177·5	214·9	248·5	279·0	303·3	324·7	424
α .	0·467	0·566	0·654	0·734	0·798	0·854	1·000

The calculated values for the **degree of ionization** $H_2SO_3 \rightleftharpoons 2H^{\cdot} + SO''_3$ are represented by α. Sulphurous acid is a binary electrolyte, and W. Kerp and E. Bauer calculated values for the degree of ionization α_1, $H_2SO_3 = H^{\cdot} + HSO'_3$, and for α_2 : $H_2SO_3 = 2H^{\cdot} + SO_3''$ from the lowering of the f.p. δ with soln. containing M-mols of H_2SO_4 grms. of water:

M .	0·161	0·299	0·408	0·633	0·786	1·065
δ .	0·382	0·662	0·894	1·352	1·682	2·279
α_1 .	0·286	0·195	0·185	0·154	0·157	0·156
α_2 .	0·143	0·098	0·093	0·077	0·079	0·078

The first **ionization constant,** K_1, for $[H^{\cdot}][HSO_3'] = K_1[H_2SO_3]$ was calculated by W. Kerp and E. Bauer 0·0174 from the conductivity data; J. McCrae and W. E. Wilson calculated 0·017 from the partition of sulphur dioxide between chloroform and water; and K. Drucker, 0·0164 from the cryoscopic data. M. S. Sherrill and A. A. Noyes gave 0·012 expressed in terms of the activities at 25°. K. Jellinek calculated the second ionization constant K_2, for $[H^{\cdot}][SO_3''] = K_2[HSO_3']$, from the conductivity data of the alkali hydrosulphites to be three thousand times less than K_1, since $K_2 = 8{\cdot}5 \times 10^{-8}$. I. M. Kolthoff calculated $K_2 = 1 \times 10^{-7}$ at 15°. As shown by J. Linder, the laws of dilution break down with sulphurous acid, owing to internal changes in the acid—*vide supra*, absorption spectra. K. Jellinek gave 71·4 for the **ionic mobility** of SO_3''-ions; and 52 for the HSO_3'-ions. The latter value agrees with that obtained by W. Kerp and E. Bauer. L. B. Loeb studied the ionic mobility in sulphur dioxide gas; and W. G. Palmer, the effect of sulphur dioxide on the coherer in detecting electric waves.

Observations on the electrolysis of aq. soln. of sulphur dioxide were made by A. Delarive, M. Berthelot, C. F. Schönbein, G. Halphen, J. Sakurai, A. Guerout, C. Luckow, and C. F. Böhringer—*vide supra*, hyposulphurous acid. According to the conditions, there may be formed sulphur, and hydrogen sulphide at the cathode and oxidation to hyposulphurous acid, or to sulphuric acid may occur at the anode. M. Centnerszwer and J. Drucker studied the electrolysis of potassium, sodium and lithium iodides, and lithium bromide dissolved in liquid sulphur dioxide. A. Fischer and G. Delmarcel studied the **electrolytic oxidation** of sulphurous acid, using a partitioned cell with sulphuric acid or sodium sulphite as catholyte, and sulphurous acid as anolyte, and a nickel or platinum cathode, and a cylinder of platinum gauze as anode. It was found that catalysts, such as copper acetate, do not increase the yield of sulphuric acid, since the platinum of the electrode acts as the catalytic agent. Better results are obtained with low than with high concentrations of the electrolyte. When oxygen begins to be liberated at the anode, there is a sudden drop in the current strength. M. de K. and N. J. Thompson observed that sulphurous acid is easily oxidized at platinum anodes to sulphuric acid of any conc. below 95 per cent. The conc. of sulphuric acid in the cell has a great effect on the current efficiency, as also, but in a less degree, has the current density. Oxidation occurs with high current efficiencies even in conc. sulphuric acid soln. For a given conc. of sulphuric acid, the current efficiency decreases with increasing current density. K. F. Ochs observed that in the electro-oxidation of sulphurous acid the negative potential increases from $-0{\cdot}017$ to 0·131 volt, when the reaction is catalyzed by metal salts. According to H. Hoffmann, the *e.m.f.* of the gas element $SO_2 : O_2$ is smaller than expected and is incapable of furnishing large currents because of the incomplete charging of the electrodes and the small velocity of the electrode reaction. The technical possibilities of the cell for the production of sulphuric acid are therefore hopeless. The primary products of electrolysis are hydrogen and oxygen, sulphur dioxide being a secondary product.

D. F. Smith and J. E. Mayer calculated $-0{\cdot}138$ volt for the **reduction potential** of $SO_4'' + 4H^{\cdot} = SO_2 + 2H_2O$, and they gave -6350 cals. for the decrease of free energy, at 25°. Comparing this result with the values for hydrogen sulphide it follows that the reducing powers of the two gases in molar soln. are nearly the same; for higher concentrations of $H^{\cdot}$-ions the reducing power of hydrogen sulphide is the greater. Sulphur dioxide is a reducing agent in dil. acid soln., and an oxidizing agent in conc. acid soln. When a piece of platinum foil is immersed in a soln. of an oxidizing agent it acquires an electric charge, and its potential in volts, the **oxidation potential,** is a measure of the oxidizing power of the soln. S. R. Carter and F. James studied the capacity of sulphur dioxide to act as an oxidizing or reducing agent in soln. containing ferrous and ferric ions. Measurements of the electrode potentials of the half cells $Pt \mid H_2SO_4, H_2SO_3, HCl$, and $Pt \mid H_2SO_3, S, HCl$ show that with an increase in the conc. of the acid, there is a rise in the sulphur dioxide potential, and a diminution in the ferrous-ferric potential. The effect of passing from weakly acid to strongly acid soln. is to lower the oxidation potential of ferric-ferrous chlorides and phosphates, and to raise that of sulphur dioxide. The oxidation potential of cupric-cuprous chloride is actually raised by an increase in acid conc. up to about $6{\cdot}5N$, after which it decreases. In the cathodic reduction of sulphur dioxide in acid soln., hydrogen sulphide is not formed as a primary product, and it is thought that hyposulphurous acid—or possibly thiosulphuric acid, thionic acid, or an active form of sulphur—is primarily formed. A. A. Noyes and H. H. Steinour found that the e.m.f., E, of a platinized platinum electrode in soln. of sulphite-ions and $H^{\cdot}$-ions, under quiet conditions, is fairly constant, but when the soln. is agitated for a long time, E becomes negative and then gradually increases to the value for the quiescent state. The potential is not accidental; at 25°, it is given by $E = -0{\cdot}37 - 0{\cdot}0296 \log [H^{\cdot}]^{\frac{4}{3}}$; it is attributed to sulphurous acid, and a decomposition product of this acid. It is independent of the initial condition of the electrode, and is scarcely affected by the presence of sulphuric, hydrochloric, or dithionic acid. It is supposed to be hyposulphurous acid, and the nearly constant value of E is said to be due to the rate of production of this acid from sulphurous acid, being equal to the rate at which it spontaneously decomposes. The addition of sulphur has no influence on E at low temp., but at higher temp. it may affect the potential because of the accelerated rate of decomposition of the hyposulphurous acid. The potential is complicated by the presence of oxygen, since this latter assists the decomposition of the hyposulphurous acid.

W. Finkelstein measured the decomposition potentials of various substances dissolved in liquid sulphur dioxide. H. P. Cady and R. Taft studied the electrolyses of a number of soln. of salts in liquid sulphur dioxide—*vide infra.* In none of the electrolyses attempted (potassium iodate, iodide, ferricyanide, etc.) were cathodic reduction products of the electrolyte obtained. Generally, the products possessed similar qualitative properties and are considered to be produced by the discharge of the ions of the solvent. The cathodic deposit, characteristic of so many of the soln., gave reactions which indicated the presence of a sulphite, thiosulphate, and probably one or more salts of the thionic acids. Contrary to L. S. Bagster and B. D. Steel, but in agreement with M. Centnerszwer and K. Drucker, no free sulphur was contained in these deposits. Anodic products are similar to those produced in the electrolysis of the substances in aq. soln.

According to L. Boltzmann,[18] the **dielectric constant** of sulphur dioxide gas is $1{\cdot}00260$; J. Klemencic gave $1{\cdot}00905$ at $14{\cdot}7°$; and K. Bädeker, $1{\cdot}00993$ at 0° or at $\theta°$, $1{\cdot}00993 - 0{\cdot}45 \times 10^{-5}\theta + 1{\cdot}86 \times 10^{-7}\theta^2$, up to 150°. For the liquid at $14{\cdot}5°$ and $\lambda = 120$, W. D. Coolidge gave $13{\cdot}75$; and $6{\cdot}26$ at 0°; and P. Eversheim, for $\lambda = \infty$, gave $14{\cdot}0$ at 20°; $10{\cdot}8$ at 60°; $7{\cdot}8$ at 100°; $4{\cdot}5$ at 140°; and $2{\cdot}1$ at the critical temp. about $154{\cdot}2$. The dielectric constant, ϵ, of sulphur dioxide was found by C. T. Zahn to be:

	−7·5°	−5·4°	22·5°	24·2°	93·9°	170·8°
$(\epsilon - 1) \times 10^6$.	10015	9918	8176	8120	5477	3911

and the results can be represented by P. Debye's expression $(\epsilon-1)vT=0{\cdot}001433T+2{\cdot}167$, where v is the sp. vol. referred to the vol. occupied by the ideal gas at 0° and 760 mm. There is no evidence of the 10 per cent. increase observed by M. Jona at about 150°. G. Jung, and G. P. Smyth discussed the orientation of the molecules in dielectric fluids. W. Herz studied some relations between the dielectric constants and the physical properties. W. Kliefoth calculated a value for the electrical moment of sulphur dioxide, and showed that the **electrostriction,** or contraction in vol. which occurs when a powerful electric field is applied to the gas, indicates that the attraction between the molecules is of electrical origin. W. A. Macky obtained similar results in developing triboelectricity in an atm. of sulphur dioxide as in air. T. Terada and co-workers found that the sparking potential of sulphur dioxide at normal press. is three times that in air.

The chemical properties of sulphur dioxide.—According to C. Langer and V. Meyer,[19] vapour density determinations at 1700° show no evidence of the decomposition of sulphur dioxide by **heat.** H. St. C. Deville, A. Morren, A. Geitz, and P. Walden and M. Centnerszwer, however, said that when heated to about 1200°, sulphur dioxide decomposes into sulphur trioxide and oxygen. A. Winternitz found that if x denotes the percentage dissociation of sulphur dioxide, $SO_2=\frac{1}{2}S_2+O_2$, at 727°, $x=0{\cdot}0_7112$; at 1227°, 0·000138; at 1727°, 0·0148; and at 2227°, 0·240. J. B. Ferguson showed that it is probable that sulphur dioxide is less dissociated by heat than is carbon dioxide or water vapour. He calculated for the dissociation $\frac{1}{2}S_2+O_2\rightleftharpoons SO_2$, the equilibrium constant K from $[SO_2]=K[S_2]^{\frac{1}{2}}[O_2]$, $\log K=1818T^{-1}-1{\cdot}38\log T+0{\cdot}00061T-0{\cdot}0_767T^2-0{\cdot}135$. Hence, if x denotes the fraction of the original sulphur dioxide dissociated at different press. p atm.,

		1000°	1100°	1200°	1300°	1400°	1500°
K		0·350	0·030	0·0038	0·00063	0·0013	0·000031
x	$p=1{\cdot}0$	$0{\cdot}0_612$	$0{\cdot}0_661$	$0{\cdot}0_524$	$3{\cdot}0_580$	$0{\cdot}0_423$	$0{\cdot}0_459$
	$p=0{\cdot}1$	$0{\cdot}0_626$	$0{\cdot}0_513$	$0{\cdot}0_552$	$0{\cdot}0_417$	$0{\cdot}0_450$	$0{\cdot}0_313$
	$p=0{\cdot}01$	$0{\cdot}0_656$	$0{\cdot}0_528$	$0{\cdot}0_411$	$0{\cdot}0_438$	$0{\cdot}0_311$	$0{\cdot}0_327$
	$p=0{\cdot}001$	$0{\cdot}0_512$	$0{\cdot}0_561$	$0{\cdot}0_424$	$0{\cdot}0_480$	$0{\cdot}0_323$	$0{\cdot}0_359$

D. Alexejeff made calculations of the thermal dissociation of sulphur dioxide. J. Priestley, and C. L. Berthollet observed that when water and sulphur dioxide are heated in a sealed tube, sulphur is formed. A. F. de Fourcroy and L. N. Vauquelin, and C. Geitner observed no decomposition when the moist or dry gas is passed through a red-hot tube, and C. Geitner when the dry gas is heated in a sealed tube. P. Hautefeuille said that the decomposition of the moist gas in a sealed tube occurs at 440°. J. I. Pierre found that gaseous and liquid sulphur dioxide, and the aq. soln. were not changed when separately heated on a water-bath for a month, or allowed to stand at ordinary temp. for 3 years. J. Priestley observed that if sulphur dioxide and water be heated in a sealed tube, crystals of sulphur are produced. C. Geitner observed the formation of sulphur and sulphuric acid at 170°–180°; and M. Berthelot, at 150°–180°. Some sulphur may react with the water, forming hydrogen sulphide. H. Wieland found that sulphur dioxide is slowly oxidized by moist palladium, in the absence of oxygen: $H_2O+SO_2=SO_3+H_2$.

J. S. Stas [20] said that sulphur dioxide is more chemically active in sunlight than in darkness. According to P. Dutoit and E. Gyr, ordinary white **light** has no effect on thoroughly dried sulphur dioxide. J. Tyndall showed that when a beam of electric light is passed through a long tube filled with the gas, at first the gas appears to be clear and transparent, but in a few minutes the gas appears to decompose, for misty wavering striæ appear, and gradually the whole tube appears to be filled with a fog. This action of light in certain gases is sometimes called **Tyndall's effect.** In the present case the effect appears to be due to the decomposition of the sulphur dioxide, probably $3SO_2=2SO_3+S$. If left a short time in the dark the gas becomes clear, perhaps owing to the recombination of the sulphur and sulphur trioxide, or to the deposition of the fine particles on the walls of the cylinder.

Ultra-violet light from a mercury quartz lamp decomposes sulphur dioxide into its elements, a crust of sulphur being deposited on the containing mercury; the oxygen reacts with the residual sulphur dioxide. D. Berthelot and H. Gaudechon, A. Coehn and H. Becker, and H. Kühne showed that sulphur trioxide is formed when a mixture of oxygen and sulphur dioxide is exposed to ultra-violet light. A. Coehn and H. Becker found that the reaction, $2SO_2+O_2\rightleftharpoons 2SO_3$, is in equilibrium when about 100 per cent. of sulphur trioxide has been formed; whereas in the light from a mercury lamp, and at the same temperature, equilibrium is reached when 65 per cent. of sulphur trioxide has been formed. The value of the equilibrium constant K in $[O_2][SO_2]^2=K[SO_3]^2$ is $2{\cdot}9\times10^{-6}$ for light of a certain intensity, and with light of a less intensity the equilibrium constant is altered. The equilibrium point is not altered at temp. between room temp. and 800°, whereas the temp. coeff. of the thermal reaction is 1·2 for a rise of 10° between 50° and 160°. The possibility of a photochemical equilibrium, different from ordinary equilibrium, is denied by some chemists. A. Findlay observed that sulphur trioxide is formed when a mixture of sulphur dioxide and oxygen is exposed to the Tesla discharge; and W. Hallock, to radium rays—*vide infra*, the formation of sulphur trioxide.

According to E. Coehn, the photochemical decomposition of sulphur dioxide furnishes sulphur and oxygen, the latter being largely used up to form sulphur trioxide; and R. A. Hill said that the primary process involves either a dissociation of the SO_2-molecule into atomic sulphur and molecular oxygen, or simply an activation of the sulphur dioxide molecule so that the final result in either case is $3SO_2=2SO_3+S$. A. L Foley studied the effect of ultra-violet light, and of X-rays on the spectrum of sulphur dioxide. Assuming with T. von Grotthus—**2**. 18, 5—that only those rays absorbed by a substance can be photochemically active, R. A. Hill found that the absorption band commencing at $318{\cdot}2\mu\mu$ with its head at $296{\cdot}1\mu\mu$ is involved in the photochemical decomposition of sulphur dioxide. W. C. M. Lewis showed that the reactivity of a substance depends on its critical increment—**4**. 25, 8—meaning the amount of energy which must be added per molecule or gram-molecule, in excess of the average content in order to bring the molecule into the active state. The higher the critical increment, the smaller the reactivity or rate of reaction. He found that this increment appears in the term $e^{-E/RT}$ of the expression for the temp. coeff. of the velocity of the reaction, where E denotes the critical increment per mol; R, the gas constant; and T, the absolute temp. He applied the hypothesis to the thermal decomposition of sulphur dioxide. He calculated for the critical increment of oxygen 30,000 cals. per mol; for sulphur, 73,500 cals. per gram-atom; and for sulphur dioxide, 103,500 cals. per mol. Since the thermal value of the reaction, Q, can be represented by: $Q=E_{\text{resultants}}-E_{\text{reactants}}$, $81{,}400=E_{\text{resultants}}-103{,}500$, and the critical increment of the sulphur dioxide molecule is therefore 184,900 cals. This corresponds with radiation of frequency $19{\cdot}6\times10^{14}$, and wave-length $153\mu\mu$. This high value for the critical increment agrees with the great stability of sulphur dioxide even at 2200° K. The calculation assumes that atomic sulphur is concerned in the process. Remembering also that the absorption bands for oxygen—$3{\cdot}2\mu$ and $4{\cdot}8\mu$—and that the critical increment for a wave-length $4{\cdot}8\mu$ is nearly 6000 cals. per mol, if both oxygen atoms have to be activated, and if the S_2-molecule is concerned in the reaction, the critical increment for S_2+2O_2 is 33,500 cals., and the critical increment of sulphur dioxide is 95,700 cals. This agrees closely with the critical increment, 96,700 cals., calculated for the $296{\cdot}1\mu\mu$ band concerned in the photochemical reaction.

According to J. Carvallo, when a current is passed between platinum electrodes in liquid sulphur dioxide in the dark, the current-intensity falls to a constant minimum. If at this stage the liquid is alternately illuminated and darkened, the current intensity rises to a greater extent at each successive illumination, reaching a maximum at the seventh, and falls at each extinction of the light, the limit of the fall being higher at each successive extinction. These changes are shown by a curve in the original. After the final extinction the current gradually falls to the original minimum. These two effects occur in the mass of the liquid, and are produced by ultra-violet rays. The positive effect is chemical, and is due to the change represented by the equation $3SO_2=S+2SO_3$; the negative effect, which takes place in the dark, is due to the removal of the impurities by the current. This negative effect is not exhibited when an alternating current is used. J. S. Stas observed that ordinary sulphur dioxide exerts a simple reducing action on the iodate, bromate, or chlorate of silver, but sulphur dioxide which has been exposed to light exerts both a reducing action and a sulphuration similar to most of the polythionic acids. As a result silver sulphide is slowly precipitated. H. Rose noticed that sulphur dioxide obtained by the action of sulphur on manganese dioxide behaves towards silver salts differently from the gas obtained by reducing sulphuric acid with mercury or copper; and J. S. Stas observed a similar result with sulphur dioxide prepared from sulphur and sulphuric acid, but in a less degree. This does not mean that there are two different forms of sulphur dioxide, but that by certain modes of preparation, by exposing the gas in the presence of moisture to light, or by exposing the aq. soln. to light, impurities of the nature of polythionates are formed which contaminate the gas. O. Loew found that after an aq. soln. of sulphur dioxide has been exposed, in sealed tubes, to sunlight, it begins to deposit sulphur after about 2 months and at the same time forms sulphuric acid.

J. Priestley[21] found that sulphur dioxide is decomposed by **electric sparks.** He said:

> One of the most remarkable observations I have made on vitriolic acid air was that when the electric spark is taken in it, the inside of the glass tube in which it is confined is covered with a blackish substance.

The black substance puzzled him, and he finally concluded that it is *mercury superphlogisticated.* H. Buff and A. W. Hofmann showed that sulphur and sulphur trioxide are formed by the sparking; and P. de Wilde, by the silent discharge. H. St. C. Deville said that a state of equilibrium is attained, and that to decompose the gas completely the sulphur trioxide should be removed as fast as it is formed by water or conc. sulphuric acid. M. Berthelot said that some platinum sulphide may be formed on the platinum electrodes. According to M. Poliakoff, when a mixture of sulphur dioxide and oxygen is exposed to the silent electric discharge, the oxidation to sulphur trioxide is more or less completely dependent on the conc., press., etc. If the oxygen alone is subjected to the action of the discharge, it will unite with the sulphur dioxide when removed from the influence of the discharge. Sulphur dioxide, however, is not thus activated by the discharge. The results similarly obtained with various catalysts, like those of the experiments on the decomposition of potassium chlorate, point to the activation by the catalyst of the gases adsorbed by the latter. According to V. Henri and F. Wolff, the emission spectrum produced by an oscillating discharge in sulphur dioxide is attributed to the formation of **sulphur monoxide,** SO, and the energy of dissociation is estimated at 148 Cals. K. Honda and K. Otsuka calculated for the **sparking voltage** with tubular electrodes in sulphur dioxide to be for a 10-cm. gap, and a 50-cycle alternating current, 53 volts. V. T. Terada and co-workers studied the character of the sparks in sulphur dioxide.

According to M. Berthelot, dry **hydrogen** and dry sulphur dioxide react when passed through a red-hot tube, forming water and sulphur; and, if the temp. is not too high, some hydrogen sulphide is produced as well. No action occurs with the dried gases at temp. below 280°; and the moist gases do not act on one another at ordinary temp. in light. If the dried mixture be ignited in air, sulphur, hydrogen sulphide, and water are produced. The thermal value of the reaction is $SO_2+3H_2=2H_2O+H_2S+51\cdot8$ Cals.; if nascent hydrogen from zinc and sulphuric acid acts on sulphur dioxide, the thermal value of the reaction is 37·9 Cals. If a mixture of sulphur dioxide, hydrogen, and enough oxygen for the complete combustion of the hydrogen be exploded, the sulphur dioxide suffers no change. I. Traube said that the flame of a burning mixture of hydrogen and sulphur dioxide in contact with water forms free sulphur and hydrogen sulphide. The reaction $3H_2+SO_2=2H_2O+H_2S$, was studied quantitatively by M. Randall and F. R. von Bichowsky —*vide supra,* hydrogen sulphide. M. G. Tomkinson found that the reaction between the dry gases is accelerated by nickel or nickel sulphide. The whole of the sulphur dioxide is decomposed at 400°–450° if the gas current is slow. Steam, hydrogen sulphide, and sulphur are formed. Cobalt sulphide can be used as catalyst for the hydrogenation, but ferrous sulphide is not so effective. P. Neogi and B. B. Adhicary said that the hydrogen sulphide is produced with nickel as a catalyst partly by direct reduction, and partly by the reduction of nickel sulphide formed by the interaction of nickel and sulphur dioxide. According to J. H. Gladstone and A. Tribe, nascent hydrogen from the copper-zinc couple, or hydrogen from hydrogenized platinum converts sulphurous acid to sulphur, while hydrogenized palladium reduces it to hydrogen sulphide—*vide infra,* the action of metals on sulphurous acid. M. J. Fordos and A. Gélis observed that with hydrogen from dil. sulphuric acid and zinc, $3Zn+SO_2+3H_2SO_4=3ZnSO_4+H_2S+2H_2O$. H. Moissan found that sulphur dioxide reacts with the **metal hydrides**—alkali and alkaline earth metals—forming hyposulphites.

Dry sulphur dioxide is oxidized by **air** or **oxygen** only to a very small extent if at all; at an elevated temp., a little trioxide is produced, but if a contact catalyst is present, *e.g.* platinum, the oxidation readily occurs. In 1831, this was the subject of a patent by P. Phillips [22] for making sulphuric acid. The reaction was examined by S. Genelin, W. Petrie, G. Magnus, W. Rath, J. W. Döbereiner, F. Wöhler, F. Mahla, W. Hempel, etc.—*vide infra,* sulphur trioxide, and also sulphur heptoxide. E. Briner and A. Wroczynsky observed the beginnings of chemical reaction between sulphur dioxide and oxygen at a high press. E. Andreas discussed the production of electricity in the gas cell in the oxidation of sulphur dioxide by air. If the gases are dry, M. Berthelot said that oxidation does not occur at 100°, but if the gas be *in statu nascendi,* as occurs when sulphur is burnt in oxygen, or if a mixture of sulphur dioxide and oxygen or **ozone** is exposed to the silent electrical discharge, oxidation occurs. In that case, the sulphur dioxide and oxygen form some sulphur heptoxide—*vide infra,* alkali sulphites. A. Borchers found the equilibrium conditions of the reaction $\frac{1}{2}O_2 \rightleftharpoons \frac{1}{3}O_3$ to be $[O_3]^{\frac{1}{3}}=K[O_2]^{\frac{1}{2}}$, when $K=0{\cdot}1888$; and for the reaction $\frac{1}{3}O_3+SO_2=SO_3$, where $[SO_3]=K[O_3]^{\frac{1}{3}}[SO_2]$, and $K=1{\cdot}013$. With sulphurous acid, $K=0{\cdot}514$, H. B. Dixon showed that oxygen does not combine with sulphur dioxide in the presence of water-vapour at 100°, but oxidation does occur if particles of liquid water are present. According to E. J. Russell and N. Smith, when a mixture of sulphur dioxide and oxygen is allowed to stand over certain metallic oxides at the ordinary temperature, combination takes place to a certain extent between the two gases, owing to the "surface action" exerted by the metallic oxide. With the same oxide, the amount of sulphur trioxide formed depends on the extent of the surface of the oxide; and also on the state of the surface. It is least with freshly precipitated oxides which are not yet dried, and increases if the oxide has been moderately heated or kept for a long time so as to become dry. The amount is dependent on a simultaneous combination of the oxide with sulphur dioxide, and seems to proceed concurrently with this. Several cases have been observed in which sulphur dioxide was absorbed without any combination with oxygen, but no case could be discovered in which the two gases combined without a reaction taking place between the sulphur dioxide and the metallic oxide or other substance. The most striking instance of this surface action is afforded by manganese dioxide, some 20 per cent. of the sulphur dioxide being converted into sulphur trioxide. If the materials are carefully dried by means of phosphorus pentoxide, no combination takes place, as even after standing for several days no alteration in volume can be detected. By drying the mixture, combination of manganese dioxide and sulphur dioxide is thus prevented, as is also the surface action of the oxide which brings about the union of sulphur dioxide and oxygen. When sulphur dioxide and oxygen are passed over heated platinized pumice, combination diminishes as the materials are more completely dried, and can be made very small. Hitherto it has been generally held that the "contact action" of platinum could bring about combination even in the absence of any impurity, but this does not appear to be the case. J. Maisin studied the action of the electric discharge on a mixture of sulphur dioxide and oxygen whereby persulphuric anhydrides are formed.

The aq. soln. of sulphur dioxide is slowly oxidized in air, forming sulphuric acid, while C. L. Reese found that dil. soln. are rapidly oxidized. H. Rössler showed that the reaction is accelerated by copper salts; and L. Meyer, that it is accelerated in the presence of various salts, and this in the order of decreasing activity—manganese sulphate and chloride, copper sulphate, ferrous and cobalt chloride and sulphates, and the sulphates of nickel, zinc, cadmium, and magnesium; while thallous and potassium sulphates, and free sulphuric acid are inactive. J. Priestley, T. Bergman, A. F. de Fourcroy and L. N. Vauquelin, C. L. Berthollet, and C. Geitner observed that when an aq. soln. of sulphur dioxide is heated, some sulphur is formed. F. Förster and co-workers found that the autoöxidation: $3H_2SO_3=2H_2SO_4+H_2O+S$, is complete only after several days at 100° C. It is autocatalytic, being accelerated by the sulphur but retarded by the hydrogen-ions formed. It is accelerated by light and heat. F. Thomas studied the action in light. The mechanism of the change is complex, thiosulphuric and polythionic acids being formed as intermediate stages. F. Förster and co-workers consider that two different kinds of mols. must be present in the oxidation and reduction which is the first step in the process of autoxidation; they consider that these are two different forms of HSO_3'-ions or of S_2O_5''-ions reacting according to $2HSO_3' \rightarrow SO_4''+H_2SO_2$ (sulphoxylic acid); or $S_2O_5'' \rightarrow SO_4''+SO$ (sulphoxylic anhydride). As indicated in connection with the action of light on soln. of sulphurous acid and the sulphites, it may be assumed that some pyrosulphurous acid is present in soln. of sulphurous acid, and accordingly, H. Bassett and R. G. Durrant assume that the two kinds of mols. concerned in the first stage of the autoxidation are H_2SO_3 and $H_2S_2O_5$, and the reaction proceeds, $H_2SO_3+H_2S_2O_5 \rightleftharpoons H_2SO_4+H_2S_2O_4$, where hyposulphurous acid is the most probable product in the first state of the reduction of the pyrosulphurous acid. Owing to the instability of this acid proof is difficult, although E. Jungfleisch and L. Brunel, and F. Förster observed that hyposulphurous acid is formed under some conditions. H. Bassett and R. G. Durrant said the only reaction for hyposulphite in sulphite soln. undergoing autoxidation is the bleaching of indigo. F. Förster and co-workers observed that sulphur dioxide co-ordinated with thiosulphate or iodide can oxidize sulphurous acid in place of the sulphurous acid complex $H_2SO_3.SO_2$. This explains the remarkable way in which iodides or thiosulphates accelerate the autoxidation. While colourless pyrosulphurous acid, $HSO_2.O.HSO_2$, is normally responsible for the first step in the autoxidation of sulphurous acid, the pyro-form of hyposulphurous acid, $H.SO_2.O.S.OH$, is the first product of the reaction; but some pyrosulphurous acid may be transformed into the yellow complex $H_2SO_3.SO_2$, and the two forms react to produce thiosulphate and pyrosulphite: $HO.S.O.SO.OH+(HO)_2S.SO_2 \rightleftharpoons H_2S_2O_5+H_2S_2O_3$. The next stage of the reaction involves the decomposition of thiosulphuric acid (*q.v.*). F. Förster and co-workers assume that the thiosulphuric acid is derived directly from the sulphoxylic acid, a reaction which, according to H. Bassett and R. G. Durrant, does not occur. F. Förster and co-workers assume that pentathionic acid is the first product of the break-down of thiosulphuric acid, but H. Bassett and R. G. Durrant said that trithionic acid is first formed: $2H_2S_2O_3 \rightleftharpoons H_2S+H_2S_3O_6$, and this gradually yields tetrathionic and pentathionic acids as the conc. of the sulphurous acid diminishes with the progress of the autoxidation. The polythionic acids decompose in their turn, and the final products of the autoxidation are sulphur and sulphuric acid. On account of this polythionic acid formation during autoxidation, tri- and tetra-thionic acids are almost always present in old sulphurous acid soln., whether these have been entirely protected from atm. oxidation or not. As the thionic acids are slowly decomposed in acid soln., the amount surviving in any given case depends upon the age and composition of the soln. No separation of sulphur occurs for a long time, because the excess of sulphurous acid stabilizes both the sulphoxylic and the thiosulphuric acids by yielding with them the sulphur dioxide addition complexes. Formation of thiosulphate from sulphite and sulphur, according to the reaction : $H_2S_2O_3 \rightleftharpoons H_2SO_3+S$ is greatly facilitated as well as the formation of trithionate : $2H_2S_2O_3 \rightleftharpoons H_2S+H_2S_3O_6$; the hydrogen sulphide is removed by interaction with sulphoxylic acid : $H_2S+(HO)_2S \rightleftharpoons 2S+2H_2O$, with pyrosulphurous acid : $H_2S_2O_5+H_2S \rightleftharpoons S(OH)_2+HO.S.O.S.OH$, or with the sulphur dioxide of the complex $H_2S_2O_3(SO_2)_n$, thus : $H_2S+[SO_2]=S+S(OH)_2$. While the thiosulphate is forming during the autoxidation of sulphurous acid, the acidity or hydrogen-ion conc. increases, and addition of acid is consequently unfavourable to the reaction. On this account, pyrosulphite soln. undergo autoxidation much more rapidly than do sulphurous acid soln. This effect of the hydrogen ion is connected with its influence on the equilibria $H^{\cdot}+HSO_3' \rightleftharpoons H_2SO_3=H_2O+SO_2$. The more acid the soln., the greater the proportion of sulphur dioxide present, and since the autoxidation becomes correspondingly slower, this favours the view that sulphur dioxide is not one of the primary reactants. Various liquids other than water were shown by E. Matthews to favour the reaction with hydrogen sulphide and sulphur dioxide ; and the assumption that pyrosulphurous acid is one of the primary products of the reaction is supported by G. M. Bennett's observation that sulphur, or even hydrogen sulphide, was liberated when sodium sulphite or pyrosulphite, in the solid state or in sat. soln., was added to hot conc. sulphuric or phosphoric acid. Sulphur dioxide or its sat. soln. in water do not act in this way. In conclusion, H. Bassett and R. G. Durrant added that the reduction of sulphurous acid in aq. soln. probably proceeds normally to hyposulphite, and not directly to sulphur or hydrogen sulphide. These substances are products of the reduction of hyposulphurous, sulphoxylic, or thiosulphuric acid. The various reactions between metal salt soln. and sulphurous acid indicated below emphasize this hypothesis. H. Thomas discussed the oxidation of sulphur dioxide in sulphuric acid soln.

F. Förster showed that the spontaneous decomposition of sulphurous acid is autocatalytic, and is accelerated by the presence of selenium. The first products of the reaction are sulphate and trithionate ions, but not tetrathionate : $4HSO_3' \rightarrow SO_4''+S_3O_6''+2H_2O$. The slower the reaction the greater is the decomposition of the trithionate according to the equation $S_3O_6''+H_2O \rightleftharpoons SO_4''+S_2O_3''+2H^{\cdot}$. The autocatalytic nature of the main reaction is ascribed to the hydrogen ion, of which the concentration increases more rapidly than is indicated by titration, using methyl-orange as indicator, on account of the disappearance of HSO_3'. The mechanism of the process is as follows : the seleno-dithionate ion, formed rapidly by the action of hydrogen sulphite soln. on selenium or on selenious acid, undergoes decomposition, accelerated by the hydrogen ion, $SeS_2O_6''+H_2O \rightarrow SO_4''+SeSO_3''+2H^{\cdot}$; in presence of more hydrogen sulphite a series of reactions then takes place : $SeSO_3''+2H^{\cdot} \rightleftharpoons SeO+SO+H_2O$; $SeO+2HSO_3' \rightarrow SeS_2O_6''+H_2O$; $SO+2HSO_3' \rightarrow S_3O_6''+H_2O$. In the absence of selenium, the hydrogen sulphite ion decomposes very slowly, according to the equation $4HSO_3' \rightarrow 2SO_4''+S_2O_3''+2H^{\cdot}+H_2O$; the resulting hydrogen ions in this case also effect autocatalysis, probably through the formation of polythionates.

E. Jungfleisch and L. Brunel studied the action of heat up to 160° on aq. soln. of sulphur dioxide, sat. at 0°, and found that water and sulphur dioxide will react at temp. below 160°, and even at the ordinary temp. producing sulphur and sulphuric acid, but the reaction is much slower at the lower temp. and with more dil. soln. This production of sulphur and sulphuric acid really takes place in two stages, the first of which, resulting in the formation of hyposulphurous acid, is only noticeable at the lower temp. : $3SO_2+2H_2O=H_2S_2O_4+H_2SO_4$; followed by

$H_2S_2O_4=S+H_2SO_4$. Certain secondary reactions of a minor character take place at the same time. K. F. Ochs measured the potential of sulphurous acid against copper, manganese, iron, and cobalt salts in soln. between 5° and 65°. These agents act as catalysts in the oxidation of the acid. F. Binnecker arranged a number of salts, etc., in the order of their power to act as oxygen carriers in the oxidation of sulphurous acid: manganese sulphate, and chloride; cupric and cuprous chlorides; cupric sulphate; ferric chloride; cuprous oxide; ferrous, and cobaltous chlorides; ferrous sulphate; cupric hydroxide; copper; ferric and cobaltous sulphate; cupric oxide; nickel, zinc, cadmium, magnesium, thallous, and potassium sulphates; dil. sulphuric acid; and water. Observations were also made by L. Meyer, and H. Stelljes. According to A. E. Lange, sulphuric acid is not formed in appreciable quantities when sulphur dioxide is passed into a soln. of sucrose; but if a current of sulphur dioxide mixed with air free from carbon dioxide is passed through a flask containing a copper or iron salt as a positive catalyst, and then through a second flask containing the same salt together with a 25 per cent. soln. of sucrose, the formation of sulphuric acid is greatly diminished by the presence of sucrose. Air oxidizes aq. soln. of the sulphites, and J. I. Pierre observed that an acid sulphite after standing for a year in a closed vessel furnishes sulphur, and sulphuric and thionic acids. I. A. Bachman, and R. Lepetit and C. C. Satta observed that the normal alkali and ammonium sulphites are oxidized at about the same speed, and faster than the hydrosulphites. The retarding influence of alcohol and other organic substances was noted by S. L. Bigelow, H. N. Alyea and H. L. J. Bäckström, H. L. J. Bäckström, and A. and L. Lumière and A. Seyewetz—*vide infra*, alkali sulphites; and of ferric hydroxide, by S. Miyamoto.

C. Moureu and co-workers studied the catalytic action of some substances on the autoxidation of alkaline and acidic soln. of sodium sulphite, and, taking the two types of soln. in the order named, they found silicon retards, hastens; silica, retards, nil; silicon tetrachloride, retards, hastens; silicon tetrabromide, retards, hastens; silicon tetraiodide, retards, retards; silicon hydrotrichloride, —, retards; silicon phenyltrichloride, —, retards; silicon tetraethyl, —, retards; silicon tetraethoxide, retards, retards; silicon tetraphenyl, hastens, hastens; and boron, retards, —.

W. Omeliansky found that the organism which converts nitrites into nitrates will not oxidize sodium sulphite or phosphite. L. J. Thénard, and J. Meyer found that **hydrogen dioxide** oxidizes sulphurous acid and sulphites to sulphates; and A. Nabl represented the reaction: $2H_2SO_3+H_2O_2=2H_2O+H_2S_2O_6$; followed by $H_2S_2O_6+H_2O_2=2H_2SO_4$. F. Ferraboschi said that ozone is produced when hydrogen dioxide is added to aq. sulphurous acid, but not so with sodium or barium dioxide; nor when a soln. of sodium sulphite is used—*vide infra*, sodium sulphite. J. H. Kastle and A. S. Loevenhart said that when sulphur dioxide is oxidized by hydrogen dioxide, a labile oxide, $H.SO_2(O_2)H_3$, is first formed as intermediate compound.

F. Sestini[23] observed that below its b.p. liquid sulphur dioxide is insoluble in **water.** According to H. Davy, one vol. of water absorbs 30 vols. of the gas at 18°; J. Dalton, 20 vols. at ordinary temp.; N. T. de Saussure, 43·78 vols.; T. Thomson, 33 vols.; and T. J. Pelouze and E. Frémy, 50 vols. at 20° and 760 mm. J. Priestley found one part of water by weight dissolves 0·04 part of gas; A. F. de Fourcroy and L. N. Vauquelin, 0·143 part of gas; T. Thomson, 0·0909 part of gas at 16° and the sp. gr. of the soln. is 1·0513; and J. I. Pierre, W. M. Watts, W. T. Smith and R. B. Parkhurst, E. Freese, P. Walden and M. Centnerszwer, B. S. Neuhausen, A. Harpf, and J. C. Hudson made some observations on this subject. T. H. Sims' data were recalculated by W. Fulda. The absorbed gas does not escape on freezing, but it can be all driven off slowly by boiling the soln. F. Schönfeld gave for the solubility of the gas expressed in vols. of sulphur dioxide, reduced to 0° and 760 mm., dissolved by one vol. of water:

	0°	5°	10°	15°	20°	25°	30°	35°	40°
SO_2 .	79·789	67·485	56·647	47·276	39·374	32·786	27·161	22·489	18·766

This means that one vol. of water at 760 mm. press. between 0° and 20° dissolves $79{\cdot}789-2{\cdot}6077\theta+0{\cdot}029349\theta^2$ vols. of sulphur dioxide; and between 21° and 40°, $75{\cdot}182-2{\cdot}1716\theta+0{\cdot}01903\theta^2$. Or, one vol. of the sat. soln. contains at $\theta°$, between 0° and 20°, $68{\cdot}861-1{\cdot}87025\theta+0{\cdot}01225\theta^2$ vols. of gas; and between 21° and 40°, $60{\cdot}952-1{\cdot}38898\theta+0{\cdot}01903\theta^2$ vols. of gas. E. Wiedemann gave for the absorption coeff. $79{\cdot}789(1-0{\cdot}03268\theta+0{\cdot}000367\theta^2)$. Tables were also prepared by T. H. Sims, and L. Carius. T. H. Sims also measured the effect of press. He found that S grms. of gas were dissolved by a gram of water, at a press,

p mm.	30	40	100	200	600	1000	1300	1900	2000
$S(7°)$	0·010	0·013	0·027	0·050	0·141	0·229	0·295	—	—
$S(20°)$	—	0·007	0·016	0·030	0·083	0·137	0·178	0·259	—
$S(39{\cdot}8°)$	—	—	—	0·016	0·047	0·077	—	—	0·149
$S(50°)$	—	—	—	0·012	0·035	0·059	—	—	0·112

T. K. Sherwood, and J. Lindner also made some observations on the effect of press. on the solubility of the gas. J. D. van der Waals found that solubility S, at $\theta°$, and press. p, and a soln. of concentration C is $S=\log p/(335C-1{\cdot}5)-0{\cdot}0185\theta/(1\times\alpha\theta)$. According to F. Schönfeld, the gas behaves in accord with Henry's law, but T. H. Sims, E. P. Perman, B. S. Neuhausen and W. A. Patrick found that the solubility of sulphur dioxide in water can be represented by a formula of the type $v=k(p\sigma/p_0)^{1/n}$, where k and n are constants; v denotes the vol. occupied by the liquefied gas dissolved per gram of water; p_0, the vap. press.; p, the equilibrium gas press.; and σ, the surface tension of the liquefied gas at the given temp. W. B. Campbell compiled data on the vap. press. of aq. soln. of sulphur dioxide. The rate of escape of sulphur dioxide from its aq. soln. was studied by E. P. Perman; and the rate of absorption, by R. T. Haslam and co-workers, E. Oeman, W. G. Whitman and D. S. Davis, and W. K. Lewis and W. G. Whitman. The sp. gr. of the soln. have been indicated previously. G. Baume and A. Tykociner found that sulphur dioxide and water are only partially miscible at low temp. The region covered by the 2-liquid system extends from about 11 to 97 molar per cent. of sulphur dioxide, Fig. 46. The eutectic at which ice and the sulphur dioxide heptahydrate, $SO_2.7H_2O$, coexist in equilibrium lies at about −3°. The f.p. curve of the heptahydrate is intercepted at 12·1° by the straight line corresponding with one of the two liquid phases. The f.p. of the second liquid is −74°, and the corresponding straight line on the diagram intercepts the curve for sulphur dioxide of m.p. −72·3° at about 9·7 molar per cent. of sulphur dioxide. F. Guthrie gave −1·5° for the eutectic temp., and H. W. B. Roozeboom −2·6°. A. Geuther previously prepared the heptahydrate. P. Villard, G. Tammann and G. J. R. Krige, A. Bouzat, and E. Bouty regarded the crystals as hexahydrated; J. I. Pierre, as enneahydrated; O. Döpping, as henahydrated; and F. Schönfeld, and A. Delarive, as pentadecahydrated. The weight of evidence favours the view that **sulphur dioxide hexahydrate,** $SO_2.6H_2O$,

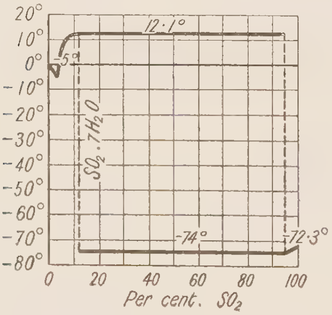


FIG. 46.—Equilibrium Diagram of Water and Sulphur Dioxide.

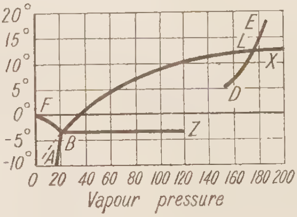


FIG. 47.—The Binary System: SO_2–H_2O (Diagrammatic).

is the actual composition of the hydrate. F. Friedrichs made some observations on this subject. O. Döpping gave −2° to −1° for the m.p.; F. Schönfeld, 3·4°; J. I. Pierre, 4°; A. Delarive, 4° to 5°; and A. Geuther, 14°. H. W. B. Roozeboom gave for the solubility of the hydrate:

	−2·6	0°	4·0°	8·0°	12·2°
Molar per cent. SO_2	2·4	2·8	3·7	5·1	11 to 96

Curve *BL*, Fig. 47, represents the equilibrium curve between the solid hydrate, a liquid soln. of sulphur dioxide in water, and vapour—sulphur dioxide and water. The vap. press. of the hydrate are −2·6° and p=211 mm.; 0° and 297 mm.; 7·1° and 760 mm.; and 12·1° and 1773 mm. The combination *BA* represents an unstable equilibrium. The curve *DL* refers to the hydrate, a liquid aq. soln. of the gas, and the vapour of gas and water:

	0°	4°	8°	12·1°
Pressure	310	495	870	1773 mm.
SO_2 in one part H_2O	0·104	0·135	0·191	0·310

The curve *LE* refers to a soln. of water in sulphur dioxide, of water in sulphur dioxide, and the vapour; and *LX*, the hydrate, soln. of sulphur dioxide in water and of water in sulphur dioxide. This curve resembles an ordinary fusion curve, and it has been followed a short way—at 12·9° and 20 atm. press.; at 14·2° and 60 atm.; at 15·3° and 100 atm.; and at 17·1° and 225 atm. At the quadruple point *L*, four phases—heptahydrate, soln. of water in sulphur dioxide and of sulphur dioxide in water, and vapour—coexist in equilibrium. The dotted curve refers to the system containing the hydrate, ice, and water—values of p and θ between −9·5° and −2·6° have been determined. The curve *BF* refers to the system ice, a soln. of sulphur dioxide in water, and vapour, and is represented by a system with ice floating in liquid sulphur dioxide; vap. press. from 0° to −2·6° have been determined. The curve *BZ* refers to a system with the 3 phases ice, solid hydrate, and a soln. of sulphur dioxide in water. At the quadruple point *B*, there are the four phases: ice, solid hydrate, a soln. of sulphur dioxide in water, and vapour.

G. Tammann and G. J. R. Krige observed only a single hydrate $SO_2.6H_2O$, which forms a eutectic with water at −2·6°. They studied the effect of press. on the hydrate in aq. soln., and their results are summarized in Fig. 48, where the curve *AB* represents the effect of press. on the m.p. of ice *I*; *CD*, the effect of press. on the water-hexahydrate eutectic; *EF*, the effect of press. on the m.p. of the hexahydrate; and *EH* is H. W. B. Roozeboom's curve of the m.p. of what he regarded as a heptahydrate. The eutectic water-hexahydrate is at −1·80° at 236 kgrms. per sq. cm. press., −2·95° at 364 kgrms. per sq. cm., and −2·00 at 270 kgrms. per sq. cm.; and the dissociation press. p, at the temp. θ, is given by $\theta=41·6(\log p+0·4904)$. G. C. and I. N. Longinescu regarded the soln. as a binary mixture of liquids in which $(CD+C_1D_1)/100$ represents the density, where C and C_1 denote the percentage concentrations, and D and D_1 the respective densities.

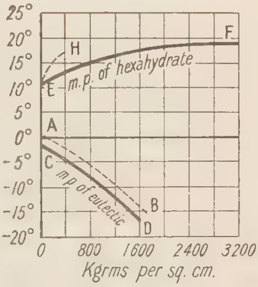


Fig. 48.—The Effect of Pressure on the Melting Point of Hexahydrated Sulphur Dioxide.

C. E. and O. Maass found for the total vap. press., p cm., of soln. of sulphur dioxide:

10°	Conc.	4·57	8·19	11·64	18·91	23·10 per cent.
	p	24·3	45·2	67·4	124·5	154·3
16·5°	Conc.	4·48	8·03	11·42	18·57	22·71 per cent.
	p	31·0	57·2	84·4	151·9	188·4
22°	Conc.	4·40	7·88	11·17	14·04	18·22 per cent.
	p	37·8	69·3	102·2	132·6	178·3
27°	Conc.	4·32	7·71	10·95	17·85	21·86 per cent.
	p	44·8	81·0	118·3	206·9	255·6

The vapour press. of the two-phase system sulphur dioxide and water is :

	10·0°	11·3°	16·5°	22·7°	27·0°
p	166·6	175·2	209·8	258·9	297·3

The effect of salts in aq. soln. on the solubility of sulphur dioxide in water has been investigated by C. J. J. Fox. In the case of sodium chloride and sulphate, and of cadmium chloride, bromide and sulphate, the solubility of the gas is lowered by the presence of the salt in soln., but in the case of the other salts, the solubility is increased owing, presumably, to the formation of complexes with the gas.

The results are expressed in terms of the ratio of the vol. of gas absorbed at the given press. and temp. to the vol. of the absorbing liquid. The value for water at 35° is 22·43, and at 25°, 32·76. The following data refer to $3N$-, $2N$-, and $\frac{1}{2}N$-soln. respectively : *potassium iodide*, 45·43, 38·04, and 26·30 at 35° ; and 68·36, 56·75, and 38·66 at 25° ; *ammonium bromide*, 52·25, 46·06, and 36·28 at 25° ; *potassium bromide*, 36·14, 31·93, and 24·83 at 35°, and 52·26, 44·96, and 35·94 at 25°. C. J. J. Fox found for $3N$-, $2N$-, and $\frac{1}{2}N$-soln. of *sodium bromide*, respectively 37·74, 36·26, and 33·76 at 25° ; *ammonium chloride*, 42·78, 39·76, and 34·58 at 25° ; *potassium chloride*, 30·02, 27·94, and 23·74 at 35°, and 42·27, 39·32, and 34·42 at 25° ; *sodium chloride*, 31·36, 31·76, and 32·46 at 25° ; *potassium thiocyanate*, 42·94, 35·05, and 25·63 at 35°, and 61·26, 51·86, and 37·57 at 25° ; *ammonium thiocyanate*, 61·46, 52·26, and 37·78 at 25° ; *sodium thiocyanate*, 48·34, 43·37, and 35·44 at 25° ; *ammonium nitrate*, 27·43, 25·57, and 23·35 at 35°, and 39·14, 37·27, and 33·96 at 25° ; *potassium nitrate*, 27·33, 25·72, and 23·27 at 35°, and 38·52, 36·66, and 33·80 at 25° ; *ammonium sulphate*, 24·60, 23·93, and 22·91 at 35°, and 35·96, 34·95, and 33·35 at 25° ; *potassium sulphate*, —, —, 33·20 at 25° ; and *sodium sulphate*, 19·27, 20·20, and 21·88 at 35°, and 28·44, 29·51, and 31·96 at 25°. C. J. J. Fox gave for $3N$-, $2N$-, and $\frac{1}{2}N$-soln. of *cadmium iodide*, respectively 24·30, 23·71, and 22·75 at 35°, and 35·77, 34·74, and 33·27 at 25° ; *cadmium bromide*, 19·17, 20·60, and 21·88 at 35°, and 27·46, 29·27, and 31·90 at 25° ; *cadmium chloride*, 18·68, 20·02, and 21·73 at 35°, and 26·06, 28·16, and 31·66 at 25° ; *cadmium sulphate*, 16·25, 18·31, and 21·45 at 35°, and 23·76, 26·58, and 31·11 at 25°. J. C. Hudson also measured the solubility of the gas in aq. soln. of potassium chloride and sodium sulphate, and showed that the results are probably affected by the tendency of the salt to hydration, and to combination with the gas as observed by C. J. J. Fox, and E. Péchard. There is a maximum in the solubility curve for sodium sulphate at 30°. Expressing the conc. of the soln. as p grms. of sodium sulphate per 100 grms. of water, the solubilities S grms. SO_2 per 100 grms. of water, are, at 30° :

p	0	2·04	3·39	5·47	7·83	10·00	20·01
S	7·608	7·709	7·776	7·773	7·716	7·586	7·006

P. Riou and P. A. Bérard observed that the rate of absorption of sulphur dioxide by milk of lime and of lime-water of various concentrations increases from the moment of separation of solid matter at a rate proportional to the conc. of the latter and decreases gradually with rise of temp. ; they also studied the rate of absorption of the gas by sat. soln. of magnesium hydroxide. H. P. Cady and R. Taft found that liquid sulphur dioxide is not nearly so good a solvent for salts as is liquid ammonia or water. The following salts are appreciably soluble in liquid sulphur dioxide : potassium chlorate, bromate, iodate, sulphide, dichromate (slightly), and ferricyanide ; sodium thiosulphate (slightly), and cyanide (slightly) ; barium dioxide ; calcium chlorate ; silver nitrate ; and cerium nitrate. The following salts, etc., are insoluble in that menstruum : potassium perchlorate, permanganate, acetate, and chromate ; sodium ; ammonium molybdate ; calcium nitrate and phosphide ; chromic oxide ; and boric acid.

O. Hartmann[24] found that steam reacts with sulphur dioxide, forming hydrogen sulphide. The stability of aq. soln. of sulphur dioxide in air is discussed above. The *autoreduction* of aq. soln. of sulphur dioxide : $3H_2SO_3=2H_2SO_4+S+H_2O$, observed by M. Berthelot, is a slow process unless the temp. be elevated, or the soln. be exposed to sunlight ; A. Geuther, and E. Divers, also observed that soln. of sulphites, hydrosulphites, and pyrosulphites undergo a similar action at 150°–200°, although G. A. Barbaglia and P. Gucci observed none during 8 hrs. at 140°. Thiosulphate appears as an intermediate product of the reaction. E. Jungfleisch and L. Brunel—*vide supra*—observed hyposulphite as an intermediate product of the reaction. G. M. Bennett observed that if sulphurous acid be liberated from its salts at 100°–120°, or lower, it undergoes instantaneous autoreduction: $4H_2SO_3 = H_2S + 3H_2SO_4$—analogous to the reaction with a sulphite $4Na_2SO_3 = Na_2S + 3Na_2SO_4$ at 150°—this reaction is an intermediate stage in the formation of free sulphur. It does not occur unless the sulphurous acid be liberated from its salts; and it may be due to the momentary existence of the asymmetric acid $H.SO_2.OH$. According to F. Förster and co-workers, the equation given by previous workers: $3H_2SO_3 \rightarrow 2H_2SO_4 + S + H_2O$, may be taken to represent the decomposition of an aq. soln. of sulphur dioxide, and G. A. Barbaglia and P. Gucci represented the reaction with sat. soln. of the hydrosulphites of sodium, ammonium, and magnesium which behave similarly at 150°: $3NaHSO_3 \rightarrow Na_2SO_4 + NaHSO_4 + S + H_2O$. The soln. of sodium hydrosulphite had suffered no change at the end of 8 hrs. at 140°. P. Klason, and T. Kiaer noticed that the presence of free sulphur, selenium, or selenium dioxide accelerated the decomposition of the aq. soln. F. Förster and co-workers said that the reaction (*a*) $3H_2SO_3 \rightarrow 2SO_4'' + 4H^{\cdot} + S + H_2O$ is very slow, requiring many days for completion at 100°, and 2 days at 150°. It is accelerated catalytically by the sulphur which is formed, but retarded catalytically by the acid produced in the reaction. The positive catalysis of the sulphur, evident at the beginning of the reaction, is soon exceeded and masked by the negative catalysis of the acid. As a result, dil. soln. decompose more quickly than conc. soln., and the decomposition is practically complete, whereas, with conc. soln., even after heating to 180°, the decomposition is incomplete, and is suppressed when $2N$-HCl is the solvent. The first stage of the reaction, supposed to be (*b*) $2HSO_3' \rightarrow SO_4'' + SO + H_2O$, is very slow, and there then follows: (*c*) $2SO + H_2O \rightleftharpoons S_2O_3'' + 2H^{\cdot}$. The sulphur catalyzes by generating thiosulphuric acid: (*d*) $HSO_3' + S \rightleftharpoons S_2O_3'' + H^{\cdot}$ far more rapidly than the speed of the two reactions which immediately precede. The thiosulphuric acid gives rise to pentathionic acid: (*e*) $5S_2O_3'' + 6H^{\cdot} \rightarrow 2S_5O_6'' + 3H_2O$, which is degraded by the sulphurous acid to tetrathionic and trithionic acids: (*f*) $S_5O_6'' + HSO_3' \rightarrow S_4O_6'' + S_2O_3'' + H^{\cdot}$, and (*g*) $S_4O_6'' + HSO_3' \rightarrow S_3O_6'' + S_2O_3'' + H^{\cdot}$, and finally, the trithionic acid is hydrolyzed (*h*) $S_3O_6'' + H_2O \rightarrow SO_4'' + S_2O_3'' + 2H^{\cdot}$. All the reactions (*c*) to (*h*) are rapid in comparison with (*b*), and they regenerate S_2O_3'', so that thiosulphuric acid is the real positive catalyst if the acid conc. is sufficient to form the pentathionic acid as in (*e*). Hence, thiosulphuric acid is always present, and the conc. of the polythionic acids also present exceeds that of the thiosulphuric acid. The more of these intermediate products present the greater does the ratio $S : SO_4$ lag behind the ratio 1 : 2 required by *a*. The negative action of the acids consist in destroying the positive catalyst by forcing (*d*) to the left, and so repressing (*e*) to (*h*) and bringing the reaction to a standstill. J. Volhard supposed that the strong positive catalytic effect of hydriodic acid on the decomposition is due to strong catalytic effect of the hydriodic acid over that of hydrochloric acid on the decomposition of the sulphurous acid; but, according to F. Förster and co-workers, it is really due to the formation of complex ions. The decomposition of the metal hydrogen sulphites is different from that of the acid itself in that until the decomposition is far advanced the conc. of hydrogen-ions remain low, being that of a hydrogen sulphite-sulphurous acid soln.; the change is therefore very strongly positively autocatalytic, and is greatly hastened by addition of sulphur or polythionates. If sulphur dioxide is allowed to escape from the soln., as by boiling a strong sodium hydrogen sulphite soln. in an open vessel, polythionic acids are not formed, the mechanism following (*b*) and (*c*) above being $S_2O_3'' + H_2O \rightarrow SO_4'' + H_2S$, $S_2O_3'' + 2H^{\cdot} \rightarrow SO_2 + S + H_2O$, and $2H_2S + SO_2 = 3S + 2H_2O$. Selenium and selenious acid act as powerful positive catalysts, forming the selenosulphate-ion $SeSO_3''$ in the soln. Potassium selenosulphate and selenodithionate have been prepared in the pure state, and indications of the existence of selenium analogues of the polythionic acids are obtained. The mechanism of the series of changes (*c*) to (*h*) when selenium dioxide is substituted for sulphur dioxide has been examined. Tellurium when free from selenium has no catalytic activity with regard to the decomposition of hydrogen sulphites.

The aq. soln. of sulphur dioxide has the character of an acid—it reddens blue litmus, it develops carbon dioxide with carbonates, and forms salts with bases. The dibasic acid is called **sulphurous acid,** H_2SO_3, and the salts are called **sulphites.** The acid forms a colourless liquid which smells of sulphur dioxide, and has an acid taste; it is the *spiritus sulfuris acidus,* or the *spiritus sulfuris per campanam* of the alchemists. P. Degener thought that the cold aq. soln. contains tetrabasic *orthosulphurous acid,* $S(OH)_4$, or H_4SO_4, because it requires 15·6 per cent. more potassium hydroxide for neutralization than is needed for the formation of the ordinary sulphite, K_2SO_3. If this be so, then the ordinary acid is *metasulphurous acid,* H_2SO_3, and the salts *metasulphites.* K. Drucker said that the aq. soln. contains SO_2, H_2O, H_2SO_3, and the ions SO_3'', HSO_3', and $H^{\cdot}$—*vide supra,* the electrical and optical properties of the aq. soln.

G. Lunge, and R. T. Thomson studied the behaviour of sulphurous acid and the sulphites towards litmus, methyl orange, phenacetolin, phenolphthalein, and resolic acid. In titrating sulphurous acid with alkalies, the colour indications with *litmus* are sharp and certain the moment saturation is complete; *lacmoid* is useless for sulphite titrations because of the indefiniteness of the end of the reaction; *methyl orange* is not affected by the sulphites; the hydrosulphites are neutral to *congo-red,* and this indicator is useless for sulphite titrations; with *phenacetolin,* sulphites yield mixed colours, but the change to red is abrupt at the moment saturation is complete; normal sulphites are neutral to *phenolphthalein* in hot and cold soln.; *curcumin* is useless for sulphite titrations because the end of the reaction is not sharply indicated; with sulphite titrations, 50 per cent. of the base may be titrated with a strong acid using *cochineal* as indicator; normal sulphites are slightly alkaline to *turmeric.* G. Wilson observed that liquid sulphur dioxide does not at first redden litmus, but after standing in contact with the acid for some time the paper is reddened, probably owing to the attraction of moisture from the air. I. M. Kolthoff studied the electrometric titration of the acid, Fig. 49. The gas decolorizes many vegetable colours provided moisture be present—roses, violets, paper dyed with logwood, etc. The bleaching effect of sulphurous acid is in part due to its reducing properties. Moistened red rose-leaves, or fabrics dyed with, say, "magenta" dye, when placed in the gas lose their colour. The sulphur dioxide appears to react with the colouring matter, forming sulphuric acid and hydrogen: $SO_2+2H_2O=H_2SO_4+H_2$, and the hydrogen bleaches by reducing the colouring agent. This idea is supported by the fact that the colour of many articles bleached by sulphur dioxide can be restored by exposing the article to oxidizing conditions. The yellow colour which gradually returns to bleached sponges, flannels, etc., is an example. The colour of bleached rose-leaves gradually returns when the rose-leaves are exposed to the air, or when the bleached leaves are dipped in dil. sulphuric acid. This shows that the colouring agent is not really destroyed during the bleaching. A coloured flower quickly drawn through the flame of burning hydrogen sulphide is bleached wherever the flame touches the flower; this is not the case with the flame of burning sulphur—presumably because of the absence of water vapour. Dry sulphur dioxide like dry chlorine does not bleach.

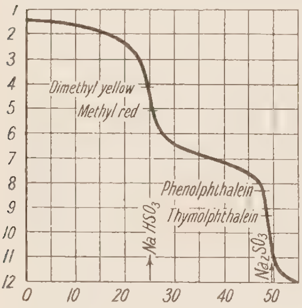


FIG. 49.—Electrometric Titration Curve of Sulphurous Acid.

H. Moissan found that **fluorine** decomposes sulphur dioxide and the products burn with a yellow flame. H. V. Regnault observed that sulphur dioxide and **chlorine** form sulphuryl chloride in sunlight; and H. L. F. Melsens showed that union occurs in darkness if the mixed gases be passed into glacial acetic acid, or if sulphur dioxide be passed over charcoal sat. with chlorine. The reaction was studied by R. H. Gerke, and H. Tramm. H. O. Schulze found other media can be used—*e.g.* camphor. J. T. Jullion oxidized moist sulphur dioxide to sulphuric acid by means of chlorine. B. Neumann and F. Wilczewsky represented the reaction with chlorine: $SO_2+Cl_2+H_2O=SO_3+2HCl$—*vide infra*, sulphuryl chloride. A. Coehn and H. Tramm found that if the gases be thoroughly dried, they do not react. An aq. soln. of sulphur dioxide reduces chlorine, forming hydrochloric and sulphuric acids: $SO_2+2H_2O+Cl_2=2HCl+H_2SO_4$. Hence sulphurous acid is used as an *anti-chlor*, that is, as an agent to remove the last traces of chlorine from articles bleached with chlorine. G. Baume and G. P. Pamfil studied the f.p. of the system: **hydrogen chloride** and sulphur dioxide, and the results are summarized in Fig. 50. The curve has a eutectic at —144·5° and 80 per cent. SO_2. H. L. F. Melsens observed that **bromine** does not unite with sulphur dioxide so readily as chlorine. The halogens oxidize sulphurous acid to sulphuric acid, forming the halogen acid. E. Léger studied the action of bromine. C. Mayr and J. Peyfuss represented the reaction: $SO_2+Br_2+2H_2O=H_2SO_4+2HBr$. F. Sestini, and F. Friedrichs observed that liquid sulphur dioxide dissolves bromine, and **iodine**—*vide infra*, sulphuryl halides. J. Fiedler found that sulphurous acid is rapidly decomposed by iodine in sunlight. The reduction of iodine by sulphur dioxide in dil. acid soln., is reversed when the conc. of the acid is over 0·05 per cent., for then hydriodic acid is oxidized to iodine. According to R. Bunsen, the oxidation of sulphurous acid by iodine is complete: $2SO_2+4H_2O+2I_2=2H_2SO_4+4HI$, provided the soln. contains less than or 0·04 per cent. of acid. This was attributed to the hydriodic acid formed in the reaction reducing the sulphuric acid: $H_2SO_4+2HI=I_2+H_2SO_3+H_2O$; but, according to J. Volhard, hydriodic acid acts as a catalytic agent in the oxidation of sulphur dioxide; involving the cyclic series of reactions: $SO_2+4HI=2H_2O+2I_2+S$; $2SO_2+4H_2O+4I=2H_2SO_4+4HI$; that is, $3SO_2+2H_2O+4HI=2H_2SO_4+S+4HI$. A little hydrogen sulphide is also formed. The reaction was studied by J. Bicskel. The iodine oxidizes sulphurous to sulphuric acid and is itself reduced to hydriodic acid. The secondary reaction can be avoided by adding the moderately dil. sulphurous acid to the standard soln. of iodine; the results are low if the iodine soln. be added to the sulphurous acid. A. Berg attributed the low results to the oxidation of sulphurous acid during the titration; he found that for each concentration of sulphurous acid, there is a limiting proportion of hydriodic acid which has no influence on the oxidation, but that the hydriodic acid has a retarding or accelerating effect according as it is present in proportions greater or less than this limit. For a 4 per cent. soln. of sulphurous acid, the limiting value is 3 per cent. HI. The amounts of oxygen absorbed by (i) sulphurous acid of this conc.; by (ii) this acid with 0·36 per cent. HI; and by (iii) this acid with 36·5 per cent. HI are as 8 : 1 : 89·5. Manganous chloride, ferrous chloride, or solutions of the metallic iodides behave similarly to hydriodic acid in accelerating the oxidation of sulphurous acid, whilst potassium chloride or bromide has no action, and hydrochloric acid retards the oxidation, and even stops it altogether. Atm. oxidation, however, is said to be a disturbing factor during the titration of sodium sulphite soln. with iodine, but R. M. Macaulay found that the low results obtained in the titration of sulphurous acid by iodine are entirely due to the escape of a portion of the sulphur dioxide during the titration; atm. oxidation is negligibly small. Sulphur dioxide was shown by F. Raschig to be more easily oxidized in the presence

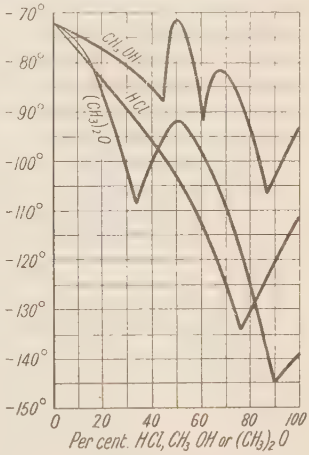


FIG. 50.—Freezing-point Curves of Binary Mixtures containing Sulphur Dioxide.

of an alkali. Contrary to E. Rupp's view, the oxidation of sodium sulphite by iodine is so fast that there is no need to allow for a time interval in the reaction. The oxidation of sulphites by iodine resulting in the formation of an iodide and sulphate was studied by A. Michaelis and G. Köthe, and W. Kalmann. The action of hydrosulphites and iodine: $2NaHSO_3+2I_2+2H_2O=2NaHSO_4+4HI$ was studied by R. Bunsen, M. J. Fordos and A. Gélis, L. P. de St. Gillés, and W. Spring and E. Bourgeois; E. Sokotoff and P. L. Maltschewsky said that some dithionic acid is formed: $2NaHSO_3+I_2=2NaI+H_2S_2O_6$. R. Otto and J. Tröger represented the reaction with a mixture of sulphides and sulphites by the equations $Na_2S+I_2=2NaI+S$; and $Na_2SO_3+S=Na_2S_2O_3$. According to R. M. Macaulay, with soln. of sulphurous acid of greater conc. than $0{\cdot}2N$-H_2SO_3, $0{\cdot}1N$-iodine gives a yellow coloration which is not due to the presence of free iodine, but to the formation of a complex $SO_2.HI$, which does not interfere with the titration. E. Péchard prepared some complexes with the gas—*vide infra*, sulphur oxyhalides. As indicated above, the increased solubility of sulphur dioxide in water containing certain salts in soln. observed by C. J. J. Fox, is attributed to the formation of complexes with the gas. The subject was studied by F. Ephraim and co-workers, P. Walden and M. Centnerszwer, and A. Adrianowsky—*vide infra*, sulphur oxyhalides. S. Zinno obtained what he regarded as iodosulphonic acid, $(HO)ISO_2$ (*q.v.*), by the action of sulphurous acid on starch iodide, or by the action of a little iodine on well-cooled sulphurous acid—*vide infra*; and **sodium iodosulphonate**—but A. Michaelis and G. Köthe said that the alleged compound does not exist. Dry **hydrogen chloride** or **hydrogen iodide** was stated by J. B. A. Dumas to react with sulphur dioxide, forming water, sulphur, and chlorine or iodine; in the presence of water, no reaction occurs. E. Briner and A. Wroczynsky observed the beginnings of a chemical reaction between sulphur dioxide and hydrogen chloride at a high press. According to A. E. Menke, sulphur dioxide and hydrogen iodide react to form sulphur monochloride (*q. v.*). S. R. Carter and N. J. L. Megson observed no complex formation between hydrogen chloride and sulphur dioxide. Soln. of sulphites are decomposed by **hydrochloric acid** with the evolution of sulphur dioxide; according to J. Hargreaves, when **sodium chloride** is heated with steam, air, and sulphur dioxide, sodium sulphate and hydrogen chloride are formed—**2**. 20, 25. H. O. Schulze said that in the presence of ferric oxide, or better cupric oxide, the reaction is quantitative at 500°. The reaction was also studied by J. Krutwig. With sulphur dioxide and steam, without oxygen, G. Keppeler and M. Hänisch found that sodium sulphite and hydrogen chloride are formed. The reaction comes to a standstill owing to its reversibility. H. O. Schulze found that a mixture of oxygen and sulphur dioxide converts heated **potassium iodide** into potassium sulphate and iodine. C. Meineke, and E. von Meyer found that **cyanogen iodide** reacts with sulphurous acid, forming sulphuric, hydriodic, and hydrocyanic acids. The oxy-halogen acids are reduced by sulphurous acids. The so-called clock reaction in the reduction of **iodic acid** and the reduction of iodates by sulphurous acid was discussed by H. H. Landolt, S. Dushman, F. Selmons, J. Eggert, R. Hoepke, L. Berceller, J. Persoz, E. Rupp and co-workers, O. Ruff and W. Jeroch, R. H. Ashley, T. Schumacher and E. Feder, A. Thiel and E. Meyer, W. S. Hendrixson, N. R. Dhar, A. Skrabal and R. Rieder, A. Skrabal and A. Zahorka, A. Skrabal, J. Eggert and L. Pfeffermann, J. Eggert, A. Thiel, G. S. Jamieson, W. R. Levinson, T. S. Patterson and W. C. Forsyth, etc.—*vide* **2**. 19, 12. H. H. Landolt represented the conc. of the sulphurous acid, by C_s and the conc. of the iodic acid by C_I, and hence found that the time of the reaction in seconds is $524{\cdot}35C_s^{-0{\cdot}904}C_I^{-1{\cdot}642}+70{\cdot}0(C_s^{-0{\cdot}904}C_I^{-1{\cdot}642})^2$. R. Hoepke deduced relative values for the affinities of various acids from their effects on the time in H. H. Landolt's reaction. According to W. S. Hendrixson, the oxidation of an acidic soln. of a sulphite with iodate involves a slow reaction: $IO_3'+3SO_3''=I'+3SO_4''$; followed by a reaction: $IO_3'+6H^{\cdot}+5I'=3I_2+3H_2O$, which is slow at first, but becomes faster as iodine accumulates in the soln.; and an instantaneous reaction: $3I_2+3SO_3''+3H_2O=6H^{\cdot}+6I'+3SO_4''$. T. W. Richards and A. L. Loomis found that the reaction is not accelerated by high frequency sound waves. W. R. Levinson discussed the catalytic action of sodium thiosulphate. W. R. E. Hodgkinson and J. Young found dry sulphur dioxide reacts with **chlorates,** forming sulphates with the evolution of chlorine peroxide which at temp. above 60° decomposes with a flash, and the formation of sulphur trioxide. Moist sulphur trioxide acts more vigorously than the dried gas, but, in most cases, without the visible liberation of chlorine peroxide. Dropping some alcoholic or ethereal soln. of sulphur dioxide on to powdered potassium chlorate causes the evolution of white fumes and a sharp explosion. W. Feit and C. Kubierschky found that **bromic acid** completely oxidizes sulphurous acid to sulphuric acid. The action of bromates was studied by W. S. Hendrixson, and he attributed the incompleteness of the reaction in acidic soln. to the formation of some dithionate.

Liquid sulphur dioxide was found by F. Sestini,[25] and F. Friedrichs to dissolve a little **sulphur.** Sulphur dioxide and sulphurous acid do not react with sulphur, although H. Debus said that with sulphurous acid an insignificant amount of pentathionic acid is formed; but A. Colefax found that in darkness at ordinary temp., and more rapidly at a higher temp., there is formed not pentathionic acid, but rather dithionic, trithionic, or tetrathionic acid. E. Bellamy found that when the sulphites are boiled with sulphurous acid, thiosulphate and trithionate are formed. The action of **hydrogen sulphide** on sulphur dioxide has been discussed in connection with the former. J. Stingl and T. Morawsky found that hydrogen sulphide decomposes sulphurous acid, forming pentathionic acid and sulphur, while W. Spring, and H. Hertlein noted the formation of sulphur, tetrathionic and dithionic acids—*vide infra,* polythionic acids. For the action on **sulphuric acid,** *vide infra,* sulphuric acid. H. Ritter observed that with **alkali sulphides,** sulphates are produced; and J. Volhard, that sulphur, sulphate, and hyposulphite are formed; and A. Guerout, that with the **metal sulphides,** sulphurous acid does not alter cupric, silver, aurous, mercuric, and platinum sulphides; zinc, manganese, and iron sulphides are readily dissolved; while cadmium, tin, arsenic, antimony, bismuth, cobalt, and nickel sulphides are sparingly soluble. If the sulphite which is first formed is soluble in water, or sulphurous acid, a thiosulphate, sulphur, and hydrogen sulphide are produced: $MS+SO_2+H_2O=MSO_3+H_2S$; $2H_2S+SO_2=2H_2O+3S$; and $3S+MSO_3=MS_2O_3+2S$. If the sulphide is sparingly soluble, or the resulting sulphite is insoluble—*e.g.* with lead sulphide—only a little thiosulphate is produced, but much sulphite and sulphur are formed. If sulphurous acid be added drop by drop to water with manganese sulphide in suspension, so that the acid is never in excess, the reaction is $MnS+SO_2+H_2O=MnSO_3+H_2S$. W. E. Henderson and H. B. Weiser discussed the action of sulphurous acid on the sulphides or iron, manganese, and zinc—*vide infra,* zinc thiosulphate—while J. Milbauer and J. Tucek found that at temp. between 300° and 800°, Ag_2S, PbS, HgS, CuS, CdS, Bi_2S_3, As_2S_3, Sb_2S_3, SnS, NiS, CoS, FeS, MnS, ZnS, cryst. Cr_2S_3, Al_2S_3, BaS, CaS, MgS, Na_2S, all prepared artificially, and pyrites, galena, zincblende, and antimonite, sodium sulphide and the alkaline earth sulphides all gave sulphates and sulphur without side-products. Al, Cr, Zn, Mn, Fe, Co, Ni, Cd, and Sn sulphides also gave sulphates, but at temp. where the sulphates decomposed with the formation of oxides, Sb, Bi, Cu, and Pb sulphides gave sulphates and the metal. Silver sulphide gave only the metal. Mercuric sulphide sublimed undecomposed at 300°–400°. C. W. Hofmann observed that sulphur dioxide acts on red-hot calcium sulphide, forming the sulphate and sulphur. L. Wöhler and co-workers found that sulphur dioxide at temp. below 1000° acts on calcium sulphide, forming the sulphate and sulphur, but the reaction is soon brought to a standstill owing to the formation of a protective film of sulphate on the pieces of sulphide. By working at temp. above 1000°, this can be avoided, as the reaction products are lime and sulphur. The low temp. reaction can, however, be accelerated by the addition of triferric tetroxide, which acts as a catalyst. Zincblende reacts with sulphur dioxide to give the oxide and sulphur, but here again the reaction velocity rapidly diminishes owing to the formation of a protective layer of basic sulphide. Both the sulphides of iron react with sulphur dioxide to give triferric tetroxide and sulphur. The reaction is rapid and complete, and is catalytically accelerated by the oxide. E. Divers and T. Shimidzu found that with **hydrosulphides,** thiosulphates are produced. A. C. Schultz-Sellack observed that liquid sulphur dioxide is miscible with liquid **sulphur trioxide,** but not with **sulphuric acid ;** F. Friedrichs found that 95 per cent. sulphuric acid has a limited miscibility at room temp. G. Lunge observed that with gaseous sulphur dioxide, the absorption coeff. for sulphuric acid of sp. gr. 1·84 is 28·86 at 16°, and 28·14 at 17°. J. Kolb found that conc. sulphuric acid of sp. gr. 1·841 absorbs 0·009 times its weight, or 5·8 times its vol. of sulphur dioxide, and the sp. gr. is thereby reduced to 1·837 ; the gas is more soluble in dil. sulphuric acid, and this the more dil. the acid. Thus :

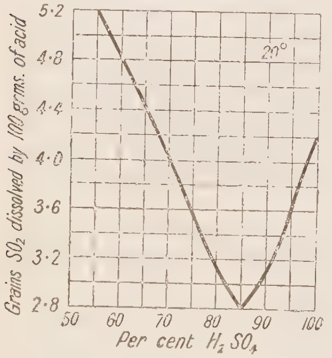


FIG. 51.—The Solubility of Sulphur Dioxide in Sulphuric Acid.

Sp. gr. H_2SO_4 . .	1·841	1·839	1·540	1·407	1·227	1·020
SO_2, grams per gram .	0·009	0·014	0·021	0·032	0·068	0·135
SO_2, litres per litre .	5·8	8·9	11·2	15·9	29·7	49·0

For sulphuric acid of greater conc. than 55·1 per cent. H_2SO_4, at 20° and 760 mm., the number of grams, *S*, of sulphur dioxide dissolved by 100 grms. of acid was found by F. D. Miles and J. Fenton to be :

H_2SO_4 .	55·1	74·1	84·2	88·1	94·0	96·5	98·5 per cent.
S . .	5·13	3·63	2·88	2·90	3·31	3·83	4·03

The solubility reaches a minimum with 86·0 per cent. H_2SO_4—the hydrate $H_2SO_4.H_2O$ contains 84·5 per cent. H_2SO_4—as illustrated by Fig. 51. V. Cupr also found a minimum at conc. corresponding with $H_2SO_4.H_2O$. He added that the minimum flattens at 60° to 65°. The changes in the absorption are connected with the formation and dissociation of a hydrate since no minimum occurs with the isotherms for acetic acid, which forms no hydrate in aq. soln. J. T. Dunn found for the coeff. of absorption (760 mm.) of sulphuric acid of sp. gr. 1·84 :

	0°	10°	20°	30°	50°	60°	80°	90°
Sp. gr. sat. soln.	—	1·8232	1·8225	1·8216	1·8186	1·8165	1·8112	1·8080
Coeff. absorption	53·0	35·0	25·0	18·0	9·5	7·0	4·5	4·0

F. Sestini found that liquid sulphur dioxide dissolves no sulphuric acid. Soln. of sulphites are decomposed by sulphuric acid with the evolution of sulphur dioxide. H. Prinz observed that liquid sulphur dioxide is miscible with **sulphur monochloride,** but no chemical action occurs at 100°. H. O. Schulze found that **sulphuryl chloride** dissolves 0·323 times its wt., or 187 times its vol. of sulphur dioxide. T. P. van der Goot studied the f.p. curve of mixtures of sulphur dioxide and sulphuryl chloride—*vide* Fig. 50. Sulphur dioxide produces red selenium by its reducing action on **selenious acid,** and black tellurium from **tellurous acid.** The reaction with selenious acid is discussed in connection with the selenothionic acids.

J. W. Dobereiner[26] observed that amidosulphonic acid (*q.v.*) is produced when dry sulphur dioxide reacts with dry **ammonia;** according to E. Divers and M. Ogawa, the dry gases do not unite at ordinary temp., but with moist ammonia gas there is a vigorous reaction ; and with a cold, dry, alcohol-free ethereal soln. of ammonia, sulphur dioxide forms ammonium amidosulphonate (*q.v.*). According to F. Ephraim and H. Piotrowsky, three different products are obtained in the action between sulphur dioxide and ammonia, (i) with an excess of sulphur dioxide—amidosulphonic acid ;

and (ii) with an excess of sulphur dioxide, either ammonium amidosulphonate, or imidodisulphinate, $NH_4.N:(SO_2.NH_4)_2$. The reaction was also examined by M. Ogawa and S. Aoyama. Sulphurous acid and aq. ammonia produce ammonium sulphites (*q.v.*). F. Raschig observed that with an acidic soln. of **hydroxylamine,** amidosulphonic acid is formed: $NH_2OH.HCl+H_2SO_3=NH_2.HSO_3+H_2O+HCl$. C. A. L. de Bruyn, A. P. Sabanéeff, and A. W. Speransky found that sulphur dioxide reacts with an aq. soln. **hydrazine** producing hydrazine sulphites (*q.v.*). F. Ephraim and H. Piotrowsky found that when sulphur dioxide is slowly passed into a soln. of hydrazine in absolute alcohol, white crystals of the hydrazine salt of hydrazine disulphinic acid are formed, *viz.*, $N_2H_2(SO_2.N_2H_5)_2$. J. Pelouze noticed that 2 vols. of **nitric oxide** and one vol. of sulphur dioxide, confined over water for a few hours, form sulphuric acid and one vol. of nitrous oxide; and, added P. Weber, the reaction is not complete in 14 days at 22·5°. G. Lunge found that dry nitric oxide does not act on dry sulphur dioxide, but the action is very marked in the presence of moisture, and nitrous oxide, but no nitrogen is formed. The gases do not react in contact with sulphuric acid of sp. gr. 1·45, but there is a contraction owing to the solvent action of the acid; but traces of nitrous oxide are formed with an acid of sp. gr. 1·32. If nitric oxide, sulphur dioxide, and oxygen act on one another in the presence of water, a trace of nitrous oxide is formed. T. L. Bailey said that sulphurous acid slowly reduces nitric oxide to nitrous oxide in the presence of sulphuric acid of less conc. than 1·07. F. Raschig observed the formation of nitrosulphuric acids when nitric oxide is absorbed by soln. of sulphites. He also found that in the presence of water **nitrogen peroxide** does not act on sulphur dioxide, but the peroxide reacts with the water, forming nitric and nitrous acids, and the latter reacts with the sulphurous acid as indicated below. L. H. Friedburg obtained nitroxylsulphuric acid by the action of dry sulphur dioxide on a soln. of nitrogen peroxide in carbon disulphide. R. Weber reported nitrosylsulphuric acid (*q.v.*) to be formed by the action of nitrogen peroxide on sulphurous acid in the cold; and nitroxylsulphuric anhydride (*q.v.*) by passing a mixture of sulphur trioxide and nitrogen peroxide through a red-hot tube. The reaction was studied by E. Briner and co-workers, G. H. Lunge, W. Manchot and H. Schmid, and C. W. H. Jones and co-workers—*vide* **8.** 49, 63.

R. Weber found that **nitrous acid** oxidizes sulphurous acid at ordinary temp., forming sulphuric acid. If a large proportion of water is present, some nitrous oxide is formed; with a small proportion of water, nitric oxide is produced; this is also the case when sulphur dioxide is passed into a soln. of nitrous acid in sulphuric acid of sp. gr. 1·4—if conc. sulphuric acid is used, the sulphur dioxide is not changed. The reactions were studied by F. de la Provostaye—*vide* sulphuric acid. E. Frémy found that in the cold, a nitrosulphuric acid—*vide* **8.** 49, 62—is produced when sulphurous acid acts on nitrous acid, and when heated, nitric oxide, nitrous oxide, and ammonia are formed. F. Kuhlmann added that some nitrogen is produced at the same time—A. Claus doubted if the nitrosulphuric acid of E. Frémy is formed under these conditions; and F. Raschig questioned if sulphurous acid is oxidized directly by nitrous acid; he assumed that the oxidation occurs through a series of intermediate stages: $HO.NO\rightarrow NO(HSO_3)\rightarrow HO.N(HSO_3)_2\rightarrow HO.NH(HSO_3)\rightarrow HN(HSO_3)_2\rightarrow H_2N(HSO_3)$. T. L. Bailey found that sulphurous acid in excess acts on nitrous acid with the evolution of nitrous oxide, and the production of hydroxyamidosulphonic acid, $(HO)NH(HSO_3)$; and with an excess of nitrous acid, nitrous oxide is produced, and if sulphuric acid be present, the nitrous oxide is progressively replaced by nitric oxide, and no nitrous oxide is formed with an acid of sp. gr. 1·225 or more. According to R. F. Carpenter and E. Linder, when sulphurous and nitrous acids interact in aq. soln. at 15° and within certain limits of conc., in the presence of excess of sulphurous acid, reactions proceed according to the three following equations: (*a*) $2NO.OH+2H_2SO_3=N_2O+2H_2SO_4+H_2O$; (*b*) $NO_2H+2H_2SO_3=OH.N(SO_3H)_2+H_2O$; (*c*) $OH.N(SO_3H)_2+H_2O=OH.NH.SO_3H+H_2SO_4$. When aq. soln. of sulphurous and nitrous acids are mixed, the acid recovered by titration is in every case less than the sum of the acidities of the acids taken, whether the titration be performed at once or several days after mixing. Nitric oxide gas is not evolved at any period of the reaction. E. Frémy, C. E. Claus, E. Berglund, and F. Raschig studied the formation of salts of the nitrosulphuric acids (*q.v.*) when sulphites act on **nitrites.** E. Divers and T. Haga said that normal sulphites and nitrites do not usually react, but F. Raschig found that there is a feeble reaction: $NaNO_2+3Na_2SO_3+2H_2O=4NaOH+N(NaSO_3)_3$, and the alkali produced hinders the further progress of the reaction. F. Raschig showed that with the hydrosulphites, a series of intermediate reactions occurs which results in the formation of nitrilotrisulphonate: $N(OH)_3\rightarrow(HO)_2N(NaSO_3)\rightarrow(HO)N(NaSO_3)_2\rightarrow N(NaSO_3)_3$; so that the initial and final products are: $NaNO_2+3NaHSO_3=N(NaSO_3)_3+NaOH+H_2O$.

F. Raschig found that aq. soln. of **nitric acid** and sulphurous acid do not react at ordinary temp., though H. B. Yardley, and A. Smith found that with boiling soln., nitric acid may be reduced to nitrogen. According to R. Weber, nitric acid is not so readily reduced as nitrous acid by sulphurous acid. If one vol. of nitric acid of sp. gr. 1·4 be boiled with 5 vols. of sulphurous acid, nitric and nitrous acids are formed; with a smaller proportion of water, the evolution of nitric oxide commences suddenly before boiling occurs. If sulphur dioxide be passed into a mixture of conc. sulphuric acid with 10 per cent. of nitric acid, and the sat. soln. be allowed to stand for 24 hrs., crystals of nitroxysulphuric acid are deposited; if more sulphur dioxide be passed into the soln., the liquid becomes dark violet. If sulphur dioxide be passed into a mixture of nitric acid with dil. sulphuric acid of sp. gr. at least 1·34, nitric oxide is formed; if sulphuric acid of sp. gr. 1·398 mixed with one-fifth to one-sixth its vol. of nitric acid of sp. gr. 1·25, be treated with sulphurous acid, the liquid becomes deep-green, and the nitric acid is decomposed with the evolution of nitric oxide. If sulphuric acid of sp. gr. 1·44–1·496 be used, the mixture becomes blue; if the sulphuric acid has a sp. gr. 1·53, the mixture becomes grass-green or yellowish-green; if of sp. gr. 1·63, yellow; and if of greater sp. gr., colourless. Dil. nitric acid not affected by sulphurous acid is decomposed if it be dissolved in sulphuric acid. If liquid sulphur dioxide be dropped into hydrated nitric acid, red fumes are given off and nitroxylsulphuric acid is formed; the excess of sulphurous acid passes off, and a violet mass of coloured sulphuric acid remains. Nitric acid decomposes sulphites with the evolution of sulphur dioxide. W. R. E. Hodgkinson and J. Young observed that the exposure of **nitrates** to dry sulphur dioxide results in their complete conversion into sulphates with the evolution of nitrous fumes. The reaction is accompanied by a rise of temp. which occasions an explosion if the treatment is applied to gunpowder.

According to A. Vogel,[27] if a piece of **phosphorus** be kept for some weeks under sulphurous acid, it acquires a pale-yellow crust. F. Friedrichs observed that yellow phosphorus is scarcely soluble in liquid sulphur dioxide; and that red phosphorus is very slightly soluble. When sulphurous acid and phosphorus are heated in a sealed tube to 200°, A. Oppenheim found that hydrogen sulphide is produced: $H_2SO_3+3H_2O+2P=2H_3PO_3+H_2S$. F. Sestini observed that liquid sulphur dioxide dissolves a little phosphorus. Sulphurous acid and sulphur dioxide gas decompose **phosphine,** and A. Cavazzi said that at 60°–70°, the reaction progresses: $PH_3+2H_2SO_3=H_3PO_4+2H_2O+2S$; and if finely divided mercury be present, $PH_3+H_2SO_3+Hg=H_3PO_2+H_2O+HgS$. According to P. Kremers, and H. Schiff, **phosphorus pentachloride** reacts with the gas: $SO_2+PCl_5=POCl_3+SOCl_2$; A. Michaelis observed that when the gas mixed with **phosphorus trichloride** is passed through a red-hot tube, there is a reaction: $3PCl_3+SO_2=PSCl_3+2POCl_3$, and some sulphur is simultaneously formed; while L. Carius found that anhydrous sulphites react with **phosphoryl chloride,** producing thionyl chloride. E. Divers represented the reaction: $POCl_3+3Na_2SO_3=3NaCl+Na_3PO_4+3SO_2$. C. F. Schönbein observed that **phosphorous acid** forms with sulphurous acid a liquid which quickly decolorizes a soln. of indigo. F. Wöhler showed that when sulphurous acid is warmed with phosphorous acid, hydrogen sulphide and phosphoric acid are formed : $3H_3PO_3+H_2SO_3=3H_3PO_4+H_2S$; and the hydrogen sulphide reacts with the remaining sulphurous acid, forming water, sulphur, and dithionic acid. The reaction is usually represented $2H_3PO_3+SO_2=2H_3PO_4+S$; and it was studied by A. L. Ponndorf, L. Maquenne, and A. Cavazzi. A. L. Ponndorf also showed that sulphur dioxide is deoxidized by **hypophosphorous acid** ; and A. Michaelis and J. Ananoff, by **phosphenylous acid.** Soln. of the sulphites are decomposed by **phosphoric acid** with the evolution of sulphur dioxide ; similarly also with **arsenic acid.** For the reduction of **arsenates** and **arsenic acid,** *vide* these compounds. J. Uhl said that when **arsenic** or **antimony** is heated in sulphur dioxide gas, the sulphide and oxide are formed ; H. Schiff reported the sulphide alone. E. Donath found that while stannous chloride is oxidized to stannic chloride in a strongly acidified soln., **arsenic trichloride** and **antimony trichloride** are not affected, and he applied the facts to the separation of tin from antimony and arsenic. J. A. Smythe and W. Wardlaw also failed to detect any evidence of reaction with arsenic and antimony trichlorides and sulphur dioxide under these conditions. When a slow current of sulphur dioxide is passed through a hot strongly acid soln. of tin, arsenic, or antimony chloride, arsenious and antimonious sulphides are precipitated, and the tin is not precipitated—this reaction was employed by N. Fedoroff for separating arsenic, antimony, bismuth, copper, and platinum sulphides from tin.

According to N. T. de Saussure,[28] 1·57 grms. or one c.c. of **wood-charcoal** absorbs, as a maximum, 65 c.c. of sulphur dioxide ; R. M. Winter and H. B. Baker found that wood-charcoal which had been heated for 4 hrs. at 900° absorbed 97 c.c. of sulphur dioxide per gram ; if heated 40 hrs., 195 c.c. were absorbed ; if heated 42½ hrs., 241 c.c. were absorbed ; and if heated 45½ hrs., 288 c.c. were absorbed. At the same time the sp. gr. of the charcoal rose from 1·76 to 1·84. A. M. Williams measured the isotherm at $-10°$ for the effect of press. on the absorption of sulphur dioxide by blood charcoal. The heat of absorption at constant vol. varies with the degree of absorption, and it is said to show maximum and minimum values. M. Polanyi and K. Welke, D. O. Shiels, O. Ruff and G. Rösner, A. S. Coolidge, and F. A. Henglein and M. Grzenkowsky studied the adsorption of sulphur dioxide by charcoal. P. A. Favre said that 165 c.c. of the gas are absorbed ; and P. Chappuis, P. A. Favre, and S. J. Gregg investigated the heat of absorption—*vide supra ;* H. Kayser found that the quantity of gas condensed by one c.c. of boxwood charcoal at p mm. press., and 19°, is $42·614–11·133 \log p$. A. G. R. Whitehouse gave 0·359–0·627 cal. for the heat of absorption per c.c. by charcoal. For wetting a gram of carbon, 0·204 c.c. of liquid sulphur dioxide is necessary. A. Reychler found that the absorption of the gas by uncalcined charcoal is complicated by the liberation of carbon dioxide and sometimes water vapour. When sulphur dioxide is passed over red-hot **carbon,** carbon dioxide and sulphur are produced. A. Eiloart also examined the reaction qualitatively ; M. Berthelot said that carbon monoxide, carbonyl sulphide, carbon disulphide, and free sulphur are produced ; and A. Scheurer-Kestner represented the reaction at a white-heat : $2SO_2+3C=2CO+CO_2+2S$; and B. Lepsius ; $SO_2+2C=S+2CO$. T. J. Drakeley found that sulphur dioxide passed over heated coal forms hydrogen sulphide. B. Rassow and K. Hoffmann observed the formation of carbon disulphide—*vide* **6.** 39, 40. M. Berthelot passed a mixture of sulphur and **carbon monoxide** through a red-hot tube and observed the formation of carbon dioxide and sulphur. E. Hänisch and M. Schröder represented the reaction $SO_2+2CO=2CO_2+S$; W. Smith and W. B. Hart found that the presence of moisture favoured the reaction. P. Winternitz, and J. B. Ferguson studied the equilibrium conditions of the reaction : $CO+\frac{1}{2}SO_2=CO_2+\frac{1}{4}S_2$. The latter observed that between 1000° and 1200°, using broken porcelain or platinized porcelain as a contact catalyst, the values of K in $[CO_2][S_2]^{\frac{1}{4}}=K[CO][SO]^{\frac{1}{2}}$ could be represented by $\log K=5659T^{-1}-0·6915 \log T+0·000307T-0·0_734T^2-0·872$, where T denotes absolute temp. The calculated values of $\log K$ are 1·75 at 1000° ; 1·43 at 1100° ; 1·15 at 1200° ; 0·90 at 1300° ; 0·69 at 1400° ; and 0·50 at 1500°. The calculated proportion of carbonyl sulphide formed by the reaction $CO+\frac{1}{2}S_2 \rightleftharpoons COS$ did not exceed 1·5 per cent., and was usually too small to determine. The thermal value of the reaction $CO+\frac{1}{2}SO_2=CO_2+\frac{1}{4}S_2$ is $-25915+1{\cdot}375T \log T-0{\cdot}0014T^2+0{\cdot}0_6155T^3+3{\cdot}99T$, or, at 25°, −22,510 cals. M. Berthelot found that at a red-heat sulphur dioxide reacts with **carbon dioxide,** forming carbon monoxide, and carbonyl sulphide; when the mixture of gases is sparked, carbon monoxide and sulphur trioxide are formed as a consequence of the reaction $CO_2=CO+O$. The sulphites are not decomposed by carbonic acid. F. Sestini found that liquid sulphur dioxide dissolves **carbon disulphide,** and the liquid is soluble in 3 vols. of carbon disulphide on warming, but separates out again on cooling. J. E. Lewis studied the viscosity of soln. of sulphur dioxide in carbon disulphide. D. Vorländer found that the action of **cyanogen** on sulphurous acid is similar to that of the halogens, but occurs more slowly; $C_2N_2+H_2SO_3+H_2O=2HCN+H_2SO_4$, with equivalent quantities in 0·1 to 0·2 per cent. soln., the amounts of cyanogen reduced and of sulphurous acid oxidized are initially equivalent. With a large excess of cyanogen, 94 per cent. of the sulphurous acid is oxidized after four to five days, but when the acids are in excess, only 23 per cent. of the cyanogen is reduced in seven to eight days.

Sulphur dioxide is more soluble in **ethyl alcohol** than it is in water. According to N. T. de Saussure, 100 vols. of alcohol of sp. gr. 0·84 absorb at 760 mm. press., 11·577 vols. of sulphur dioxide at 17°. L. Carius found that one vol. of a sat. soln. of the gas in alcohol dissolves the following vols. of sulphur dioxide gas:

	0°	5°	10°	15°	20°	25°
Vols. SO_2 .	216·40	175·36	142·22	115·78	96·44	84·20

or one vol. of alcohol at 760 mm. and at θ° dissolves $328{\cdot}62-19{\cdot}65\theta+0{\cdot}3119\theta^2$ vols. of sulphur dioxide, for the sp. gr. of the soln., and F. Isambert's measurements of its compressibility, *vide supra.* When a dil. alcoholic soln. of sulphur dioxide in alcohol is heated in a sealed tube, H. Endemann represented the reaction: $4SO_2+4C_2H_5OH=C_2H_5SH+3(C_2H_5O.SO_2.OH)$; with conc. soln., the reaction progresses in stages: $C_2H_5OH+SO_2=C_2H_5.SO_2OH$; $C_2H_5.SO_2OH+3SO_2=C_2H_5SH+3SO_3$; $3SO_3+3C_2H_5OH=3(HO.SO_2.OC_2H_5)$; and $3(C_2H_5O.HSO_3)+3C_2H_5OH=3H_2SO_4+3(C_2H_5)_2O$. S. Pagliani observed that some monoclinic sulphur separates as the mixture cools; and M. Berthelot, that if the alcoholic soln. is kept for some time, crystals of sulphur and $CH_3CO.H$ are formed. W. F. Seyer and R. W. Ball studied the f.p. of binary mixtures of liquid sulphur dioxide and **cetyl alcohol.** C. A. L. de Bruyn gave for ethyl alcohol and **methyl alcohol** at 760 mm. expressed in grams of sulphur dioxide per 100 grms. of soln.:

	0°	7°	12·3°	18·2°	26·0°
C_2H_5OH . .	53·5	45·0	39·9	32·8	24·4
CH_3OH . .	71·1	59·9	52·5	44·0	31·7

B. S. Neuhausen studied the solubility of sulphur dioxide in methyl and ethyl alcohols. G. Baume and G. P. Pamfil studied the f.p. of the system methyl alcohol and sulphur dioxide, Fig. 50, and found that the curve has three eutectics at −88°, −91·5°, and −106° respectively; and two maxima, one at −71° corresponding with $CH_3OH.SO_2$, and one at −81° corresponding with $2CH_3OH.SO_2$. A. M. Wasilieff made some observations on this subject. F. Sestini found that liquid sulphur dioxide dissolves **ether,** forming a yellow soln. J. E. Lewis studied the viscosity of soln. of sulphur dioxide in ether. G. Baume studied the f.p. of the system: **methyl ether** and sulphur dioxide, Fig. 50; there is a maximum at −91·5° corresponding with $(CH_3)_2O.SO_2$ between the eutectics at −109° and −144°. A. M. Wasilieff made some observations on this subject. F. Sestini found that liquid sulphur dioxide dissolves **chloroform.** J. Linder gave the solubility, S, of the gas in grams of sulphur dioxide per 100 c.c. of sat. chloroform soln. at different press., p mm.:

	0°					25°				
p .	2·7	5·6	22·0	90·2	219·6	5·7	12·9	48·8	200·2	488·8
S .	0·0701	0·01790	0·6982	3·097	8·217	0·0669	0·1712	0·6728	2·954	7·839

J. McCrae and W. E. Wilson found that the partition coeff. of sulphur dioxide between water and chloroform, at 20°, varies with the conc. from 1·56 at a conc. of 0·055 gram-eq. per litre in the aq. phase to about 0·9 when the conc. is 1·038 gram-eq. The partition-coeff. is, however, not directly proportional to the conc. The addition of hydrochloric acid diminishes the partition-coeff., and this is in agreement with the view that the inconstancy of the distribution ratio is due to the varying degree of the ionization of the sulphurous acid. P. A. Bond and H. T. Beach studied the binary system : **carbon tetrachloride** and liquid sulphur dioxide. The results are summarized in Fig. 52. The critical soln. temp. is at —29·3°, and both liquids are stable phases down to —45°. J. Horiuchi gave 12·49 for the solubility of sulphur dioxide in carbon tetrachloride at 40°. R. de Forcrand and S. Thomas obtained a mixed hydrate of carbon tetrachloride and sulphur dioxide. J. E. Lewis studied the viscosity of soln. of sulphur dioxide in carbon tetrachloride. H. Bunte described the compound of sulphurous acid with **acetaldehyde**—*viz.* $CH_3.CH(OH).O.HSO_3$. W. Kerp studied the compounds with acetaldehyde, **formaldehyde, benzaldehyde,** and **acetone.** J. E. Lewis studied the viscosity of soln. of sulphur dioxide in acetone. C. Bertagnini, and F. Heusler studied the action on **cinnamaldehyde ;** F. Tiemann, on cinnamaldehyde, **citronellal,** and **citral ;** and E. Knoevenagel, and E. Hägglund and A. Ringbom, on various **unsaturated organic compounds**—cinnamaldehyde, dimethylcyclohexane, carvone, ethyl ethylideneacetoacetate, phorone, allylacetone, benzylideneacetophenone, piperonylideneactone, etc. H. O. Schluze found that at 0°, and 725 mm., acetone dissolves 2·07 times its wt. or 589 times its vol. of sulphur dioxide, and there is formed a complex :

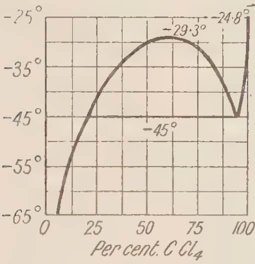


FIG. 52.—The Binary System : SO_2–CCl_4.

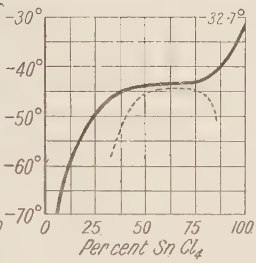


FIG. 53.—The Binary System : SO_2–$SnCl_4$.

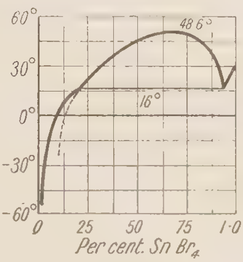
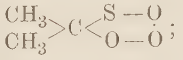


FIG. 54.—The Binary System : SO_2–$SnBr_4$.



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!C\!<\!\begin{matrix}S-O\\O-O\end{matrix};$$

G. Schmitt said that a soln. of sulphur dioxide in acetone has great solvent power for unsaturated organic compounds and resinous substances. H. O. Schulze showed that **formic acid** dissolves 0·821 times its weight, or 351 vols. of the gas. S. J. Lloyd found that at —5°, 0°, 10°, and 30°, acetic anhydride dissolves respectively 196, 148, 122, and 90 grms. of SO_2 per litre. J. Papish observed that sulphur dioxide is reduced by **methane** at elevated temp.—*vide supra*, sulphur. F. Sestini observed that liquid sulphur dioxide dissolves **benzene** when warmed. E. B. Evans and co-workers studied the action of alkali sulphites on asymmetric halogen compounds of the type CHR_1R_2X. S. J. Lloyd found that with benzene at 30°, 40°, 50°, and 60° respectively 127·5, 82·9, 60·3, and 31 grms. of sulphur dioxide were dissolved per litre of benzene ; with **nitrobenzene,** the corresponding data at 15°, 25°, 40°, and 60 were respectively 311·4, 227·9, 132, and 78·6 ; with **toluene,** at 20°, 30°, 40°, and 60°, respectively 217·5, 124·4, 93·6, and 54·7 ; and with *o*-**nitrotoluene,** at 15°, 25°, 40°, and 60° respectively 290·8, 192·2, 118·5, and 68·8. W. F. Seyer and V. Dunbar found that on the equilibrium diagram of liquid sulphur dioxide and **cyclohexane** there is a transition point at —17·0°, corresponding with the maximum solubility of sulphur dioxide in *cyclo*hexane, and of a eutectic point at —72·5°, at which temp. the solubility of *cyclo*hexane in liquid sulphur dioxide is very small. Above 13·6°, the liquids are miscible in all proportions. There is no evidence of the formation of compounds of the two substances, as suggested by R. J. Moore and co-workers. The action of sulphur dioxide on *cyclo*hexanone and on methyl*cyclo*hexanone was studied by G. Weissenberger and L. Piatti—both substances readily absorb the gas and gives off nearly all of it at 80°. If some trioxide be present, the solvents are sulphonated. W. F. Seyer and A. F. Gill found that the critical soln. temp. with liquid sulphur dioxide and *n*-**hexane** is 10·1° ; the f.p. of sulphur dioxide is lowered from —72·8° to —73·5°, and the solubility curve is similar to that for *cyclo*hexane. It is not possible to separate naphthalenes from paraffins by liquid sulphur dioxide. W. F. Seyer and J. L. Hugget found the critical soln. temp. with **cetene** or **hexadecene** is 42·7° ; and W. F. Seyler and A. F. Gallaugher found that mixtures with *n*-**octane** showed no sign of the formation of a compound. Under ordinary conditions the **diolefines** are soluble and the **mono-olefines** are insoluble in liquid sulphur dioxide. E. Hägglund and A. Ringbom studied the action of sulphites on unsaturated organic compounds. R. J. Moore and co-workers found benzene, toluene, **xylene, mesitylene,** and **olefines** were miscible in liquid sulphur dioxide in all proportions ; **paraffins** up to decane were practically insoluble ; and **naphthalene** showed a limited miscibility. J. E. Lewis studied the viscosity of soln. of sulphur dioxide in benzene, toluene, xylene, and **heptane.** P. Walden found that liquid sulphur dioxide dissolves **ammonium thiocyanate,** and the **methylammonium chlorides and bromides**—*e.g.* $(CH_3)NH_3Cl$; $(CH_3)_2NH_2Cl$; $(CH_3)_3NHCl$; $(CH_3)_4NCl$; and $(CH_3)_4NBr$—forming colourless soln. ; **methylsulphonium iodide, methylammonium and ethylammonium iodides**—*e.g.* $(CH_3)_3SI$; $(CH_3)_4NI$; and $(C_2H_5)_4NI$—forming yellow soln. ; **carbonyl thiocyanate,** forming a blue soln. S. Smiles and R. le Rossignol, C. Friedel and J. M. Crafts, E. Knoevenagel and J. Kenner, and C. E. Colby and C. S. Loughlin studied the chemical action of sulphur dioxide on benzene. Many other organic substances are soluble in the liquid. J. A. Smythe and A. Forster showed that sulphur dioxide can oxidize the **mercaptans:** $SO_2+4(C_6H_5.CH_2.SH)=2H_2O+(C_6H_5.CH_2)_2S_2+(C_6H_5.CH_2)_2S_3$. For complexes with the thiocyanate, *vide supra,* the iodides. A. Étard obtained crystals of **potassium sulphurylcyanide,** $KCy.SO_2.H_2O$, by the action of sulphur dioxide on a cold 40 per cent. soln. of **potassium cyanide.** The mother-liquor, when sat. with sulphur dioxide yields the complex **potassium sulphuryl hydrosulphitocyanide,** $KCy.KHSO_3.SO_2$. H. O. Schulze, and A. Bineau observed that **camphor** absorbs sulphur dioxide gas—the former said that, at 0° and 725 mm., it absorbs 0·880 part by wt. or 308 parts by vol. of the gas. I. Bellucci and L. Grassi studied the system : camphor–sulphur dioxide. A. Reychler said that the absorption of sulphur dioxide by camphor, and by **caoutchouc** shows a phenomenon similar to that presented by liquids with respect to Henry's law. At 18·5°, $C_1/C_2=25·8$, where C_1 and C_2 denote the number of mols of sulphur dioxide respectively in a kilogram of caoutchouc and in a litre of gas. The heat of absorption by black caoutchouc was found by P. Chappuis to be 0·000256 to 0·000245 Cals. per c.c. of gas. A. Reychler represented the adsorption of sulphur dioxide by fat-free **wool** by $C_1=0·88+4·7C_2$. W. Kerp said that the sulphur dioxide present in fruit juices and dried fruits, preserved with this substance, is in organic combination, and is gradually liberated when the aq. extract is acidified. This gradual liberation of the sulphur dioxide is also exhibited by soln. of sugars containing sulphur dioxide and also by the compound of acetaldehyde and sulphurous acid. This latter compound is also contained in **wines** treated with sulphur dioxide. In aq. soln. it is partially hydrolyzed, forming sulphurous acid and aldehyde, but even in very dil. soln. the amount of decomposition is extremely small. The velocity of combination of sulphurous acid and aldehyde depends on the conc. of the soln. In fermented wines which have had only a moderate treatment with sulphur, the combined sulphur dioxide is contained in the form of the acetaldehyde compound, but in sulphurated musts and strongly sulphurated sweet wines the excess of sulphur dioxide must be assumed to be in combination with dextrose and lævulose. Since the latter compounds are more readily hydrolyzed in aq. soln., it follows that in certain cases the sulphurous acid contained in must cannot be regarded pharmacologically as identical with that contained in wine. H. Bucherer studied the action of the sulphites on **wood,** and he found that with **tanning materials,** sulphites can act as sulphonating agents without being reduced; sodium hydrosulphite unites with **resorcinol**, but not with **trihydroxybenzene** derivatives. F. Sestini observed that **resin** dissolves in liquid sulphur dioxide; G. de Bruin, that sulphur dioxide forms a compound with **isoprene**; A. Korezynsky and M. Glebocka, with **amines**; L. Marino and A. Toninelli, with **piperidine**; F. Ephraim and C. Aellig, with the alkali salts of the **fatty acids** from formic to valeric acid, and with the **benzoates;** W. Strecker, and B. Oddo studied the action of sulphur dioxide on the **magnesium alkyl halides**; and W. Kerp, on **dextrose**; J. M. van der Zanden studied the velocity of the addition of sulphites to **maleic and fumaric acids.** W. Zimmermann, and E. Hägglund and A. Ringbom studied the action of sulphites on a number of organic compounds; and K. Dürrschnabel, on **organic dyes.**

F. de Carli obtained the following values for the solubilities of various organic compounds in liquid sulphur dioxide, where s.s. means sparingly soluble; n.s., insoluble; and m., miscible. *Benzene*, m., colourless; *toluene*, m., colourless; *ethyl benzene*, m., colourless; *nitrobenzene*, 50 per cent., yellow; *cumene*, m., yellow; *propylbenzene*, m., yellow; m-*xylene*, m., colourless; *dinitrobenzene*, 51 per cent., yellow; p-*nitrochlorobenzene*, 38 per cent., yellow; p-*dibromobenzene*, s.s., colourless; o-*nitrobenzene*, 85 per cent., orange; *cimene*, m., yellow; *mesitylene*, m., yellow-orange; *dinitrotoluene*, 40 per cent., yellow; *pseudocumene*, m., yellow-orange; *butylbenzene* (*tert.*), m., yellow; *hexachlorobenzene*, n.s.; m-*dimethylcyclohexane*, s.s., colourless; *naphthalene*, 23 per cent., yellow; *a-nitronaphthalene*, s.s., yellow; *tetrahydronaphthalene*, m., yellow; *decahydronaphthalene*, n.s.; *fluorene*, 24 per cent., yellow; *anthracene*, s.s., yellow; *phenanthrene*, 23 per cent., yellow; *dibenzil*, 28 per cent., yellow; *stilbene*, s.s., yellow; *diphenylmethene*, m., yellow; *triphenylmethene*, 16 per cent., red; *acetanaphthene*, 13 per cent., yellow; *benzyl alcohol*, m., colourless; *menthol*, 27 per cent., colourless; *benzoic aldehyde*, m., colourless; *salicylic aldehyde*, m., yellow; *anisic aldehyde*, m., yellow; *cinnamic aldehyde*, m., red; *cuminic aldehyde*, m., yellow; *acetophenone*, m., yellow; *benzylacetone*, 43 per cent., yellow; *phenic acid*, 28 per cent., yellow; *benzoic acid*, s.s., colourless; *salicylic acid*, n.s.; o-*nitrobenzoic acid*, n.s.; *sulphanilic acid*, n.s.; *phthalic acid*, n.s.; *picric acid*, 38 per cent., yellow; *tetrachlorophthalic acid*, n.s.; *cinnamic acid*, s.s.; *benzyl acetate*, m., yellow; *amyl salicylate*, m., yellow; *ethyl cinnamate*, m., colourless; *benzonitrite*, m., yellow; *benzamide*, 17 per cent., colourless; p-*toluidine*, s.s., yellow; o-*nitraniline*, s.s., orange; *acetanilide*, 26 per cent., yellow; p-*nitroanilide*, 15 per cent., yellow; *benzilidenaniline*, 53 per cent., red; *camphor bromide*, 16 per cent., colourless; *pinene*, s.s., yellow; *carvene*, m., yellow; *dimethylpyrone*, n.s.; *phenylpyrrole*, 15 per cent., yellow; *carbazole*, 3 per cent., yellow; *acridine*, s.s., yellow; *thiodiphenylamine*, 21 per cent., red; *antipyrine*, s.s., yellow; *amylene*, n.s.; *caprylene*, s.s., yellow; *hexadecilene*, n.s.; *malic acid*, insoluble; *maleic acid*, n.s.; *fumaric acid*, n.s.; *oleic acid*, n.s.; *palmitic acid*, n.s.; *stearic acid*, n.s.; *aconitic acid*, n.s.; *thiourea*, s.s., yellow; *guanidinium carbonate*, n.s.

H. Lotz[29] studied the effect of the gas on various **silicates.** According to P. Chappuis, *asbestos* and *pumice-stone* show no marked tendency to adsorb sulphur dioxide; the heat of adsorption by *meerschaum* is 0·000461 to 0·000253 Cal. per c.c. The first portions of gas adsorbed evolve more heat than the later portions. J. McGavack and W. A. Patrick found the adsorption of sulphur dioxide by the hydrogel of **silicic acid** can be represented by a modification of the ordinary adsorption equation. W. A. Patrick and C. E. Greider showed that the heat of adsorption, Q, of sulphur dioxide by silica gel can be represented by $Q=0{\cdot}316X^{0{\cdot}860}$, where X denotes the number of milligrams of sulphur dioxide adsorbed per gram of gel.

For saturation, $X=525$ mgrms., and $Q=69{\cdot}1$ cals. The net heat of adsorption is 21·2 cals. The subject was studied by E. Bosshard and E. Jaag. O. Schumann, and E. Kayser observed that sulphur dioxide is absorbed by **glass,** and P. Chappuis observed that 1 sq. mm. of glass surface, at ordinary press., by warming from 0° to 180°, absorbs 0·00058 c.mm. of the gas; and A. Faber showed that glasses and glazes adsorb sulphur dioxide from flame gases. Similarly also with firebricks. M. H. Evans and H. J. George, and D. H. Bangham and F. P. Burt studied the adsorption of sulphur dioxide by glass, and showed that the adsorbed sulphur dioxide cannot be removed from glass-wool. M. Crespi and E. Moles estimated that the walls of a litre flask at 760 mm. press. adsorb 0·00040 grm. of sulphur dioxide, and this is about 0·00013 of the weight of a litre of gas. A. Portevin found that sulphurous gases, even when dil., attack basic rocks and glasses superficially at 900° with the formation of a water-soluble deposit consisting principally of sodium sulphate with traces of calcium, potassium, and magnesium sulphates. The dissolution of such deposits in warm springs during the early post-volcanic period is a probable explanation of the origin of alkaline sulphated thermal waters.

S. Klosky and A. J. Burggraff, and S. Klosky and L. P. L. Woo, studied the absorption of sulphur dioxide by **titania.** Sulphurous acid and the hydrosulphites were found by E. Knecht to give with **titanous salts** soln. an orange or brown coloured liquid containing hyposulphurous acid. E. Knecht showed that sulphurous acid is also reduced by titanous chloride to sulphur, and J. A. Smythe and W. Wardlaw found that hydrogen sulphide is freely evolved when sulphur dioxide is passed into a warm strongly acid soln. of titanous chloride. The sulphur is produced by a secondary reaction between hydrogen sulphide and sulphur dioxide. The beginning and end stages are thus represented: $3SO_2+12TiCl_3+12HCl=12TiCl_4+6H_2O+3S$. P. A. Bond and H. T. Beach have made some observations on the system: **titanium tetrachloride** and liquid sulphur dioxide. The critical soln. temp. occurs at 11·9° with 55·80 per cent. of the tetrachloride; the results with **tin tetrachloride** are summarized in Fig. 53; there is a metastable liquid binary system below the solid-liquid solubility curve; and the results with **tin tetrabromide** are summarized in Fig. 54. Stable two-liquid systems could not be obtained with less than 20 per cent. tin tetrabromide, but metastable systems were followed as far as about 35°. At temp. below −14°, the solubility of tin tetrabromide was so slight that the eutectic could not be located. A hot soln. of **stannous chloride** was found by B. Pelletier, J. Girardin, E. Hering, E. Donath, N. Fedoroff, and H. W. F. Wackenroder, to reduce sulphurous acid to hydrogen sulphide and brown stannous sulphide is formed. M. M. P. Muir observed that when sulphurous acid is boiled with stannous chloride, sulphur and stannic chloride are produced, indicating that the sulphurous acid can act as an oxidizing agent. E. Divers represented the reaction: $2SnCl_2+SO_2=S+2SnOCl_2$; and $2SnOCl_2+4HCl=2SnCl_4+2H_2O$. The oxidation of stannous chloride by sulphur dioxide in the presence of conc. hydrochloride acid was shown by W. Wardlaw, and J. A. Smythe and W. Wardlaw to proceed quantitatively: $3SnCl_2+SO_2+6HCl=3SnCl_4+2H_2O+H_2S$. R. G. Durrant showed that the action varies with the proportion of stannous chloride, sulphurous acid, hydrochloric acid, and water in the soln.; when the hydrochloric acid is in excess, the reaction is bimolecular. For complete oxidation, the molar ratios $SnCl_2 : H_2SO_3 : HCl$ must be approximately $3:1{\cdot}55:6$; higher proportions of sulphurous and hydrochloric acids accelerate the oxidation. If the hydrochloric acid be not in excess, the reaction is slow and incomplete. The main reaction is $3SnCl_2+6HCl+H_2SO_3=3SnCl_4+3H_2O+H_2S$; and the subsidiary reaction $2H_2S+H_2SO_3=3H_2O+3S$ is next in importance; the reaction $2H_2S+SnCl_4=4HCl+SnS_2$ is manifest only with high conc. of hydrochloric acid; in the earlier stages when the proportion of sulphurous acid is low, there may be produced stannous sulphide (colloidal): $H_2S+SnCl_2=2HCl+SnS$; and there may be a slight reduction of stannic chloride, $SnCl_4+H_2SO_3+H_2O=SnCl_2+2HCl+H_2SO_4$. S. W. Young showed that complexes of hydrochloric acid and stannous chloride affect the rate of oxidation. E. S. Leaver and R. V. Thurston [30] studied the reaction $2FeSO_4+SO_2+O_2=Fe_2(SO_4)_3$. Sulphites are not decomposed by **boric acid.**

U. R. Evans discussed the corrosive action of sulphur dioxide produced by the combustion of coal gas. E. Kayser, and P. Röntgen and G. Schwietzke observed the adsorption of sulphur dioxide gas by the **metals**—*brass*, and *iron*; and P. Chappuis showed that *platinum-black* adsorbs 1·68 c.c. of the gas per gram; and 0·00527 Cal. of heat is given off. According to A. Lange, purified and thoroughly dried liquid sulphur dioxide is without action on iron at about 100°; the commercial liquid attacks iron over 70°, $2Fe+3SO_2=FeSO_3+FeS_2O_3$. According to H. Schiff, and H. Buff and A. W. Hofmann, many metals become incandescent when heated in sulphur dioxide gas, forming oxide and sulphide; *potassium* forms some thiosulphate. J. A. Smythe and W. Wardlaw say that *calcium* burns brilliantly in the gas. J. Uhl said that *copper* reacts $3Cu+2SO_2=CuSO_4+Cu_2S$, and there is also formed a white sublimate; *silver* behaves like copper, forming also a little sulphur trioxide; *gold* forms some sulphur and sulphur trioxide without the metal being attacked. A. Sieverts studied the solubility of sulphur dioxide in copper. *Magnesium* reacts with incandescence, forming sulphide, sulphite, and sulphate; there is a small action resulting in the formation of sulphide in the case of *zinc, aluminium, cobalt,* and *nickel; cadmium* behaves like copper; *mercury* and *bismuth* are not attacked. P. Neogi and R. C. Bhattacharyya observed that sulphites are not attacked by *magnesium amalgam.* S. Hilpert and E. Colver-Glauert found that sulphurous acid (1 : 25) reacts with iron coating a polished face with a layer of sulphide; cementite is not attacked. Hence, they propose to use this liquid as an etching reagent for developing the structure of iron and steel. A. Guntz observed that pyrophoric *manganese* absorbs the gas with incandescence: $3Mn+SO_2=MnS+2MnO+82{\cdot}2$ Cals. W. R. E. Hodgkinson and F. K. S. Lowndes observed that with *platinum* and *palladium* there is a reaction: $Pd+3SO_2=PdS+2SO_3$; but that red-hot platinum does not attack the gas. This agrees with J. Uhl's observation. D. O. Shiels studied the adsorption of sulphur dioxide by finely divided platinum. The observations of H. Risler-Beunat, A. Harpf, E. Mitscherlich, P. Schützenberger, and others on the action of the metals on sulphurous acid have been discussed previously in connection with the preparation of hyposulphurous acid, and also in connection with thiosulphuric and pentathionic acids (*q.v.*). C. Geitner observed that besides the acids just indicated sulphides and sulphur were formed with zinc, and cadmium; and M. J. Fordos and A. Gélis made a similar observation with respect to *tin, iron, cobalt,* and *nickel*; with *lead*, $Pb+6SO_2=PbS+S+4SO_3$. P. Schweitzer showed that with *zinc*, sulphur, thiosulphuric and trithionic acids, and zinc sulphite are formed; while cadmium, and nickel give at first sulphite, thiosulphate, and sulphur, and after standing a longer time, sulphide and sulphate; *sodium, magnesium,* and *aluminium* furnish hydrogen, sulphite, thiosulphite, sulphate, and trithionate. M. Berthelot observed that nickel and cadmium form the metal sulphide and a soluble salt; lead is blackened, but not much attacked; while *mercury* suffers no change. The observations of S. U. Pickering, C. Geitner, L. P. de St. Gilles, M. Berthelot, H. Rössler, G. Bredig, H. Reinsch, and J. Uhl on the action of sulphurous acid on *copper* have been previously discussed—**3.** 21, 6. E. Barruel observed that copper at ordinary temp. and protected from air, forms copper sulphide and sulphate when treated with sulphurous acid; H. E. Causse said that the reaction occurs in two stages—(i) cupric sulphite and hyposulphurous acid; and (ii) cupric sulphate and hydrogen sulphide, while basic sulphite appears as a result of a secondary reaction. M. Berthelot also made observations on the action of copper and silver on sulphurous acid.

E. J. Russell and N. Smith's [31] observations on the action of a mixture of sulphur dioxide and oxygen on the **metal oxides** have been previously indicated. **Sodium dioxide,** dusted into a cylinder of the gas, glows brightly owing to the heat evolved during the reaction: $Na_2O_2+SO_2=Na_2SO_4$. O. Schott observed that at 200°, **barium oxide** reacts energetically with sulphur dioxide, **strontium oxide** at 290°, and **calcium oxide** at a temp. below redness; while C. Birnbaum and C. F. Wittich found that calcium oxide at 400° reacts with sulphur dioxide, forming a basic sulphite, $CaO.5CaSO_3$, and at 500°, calcium sulphate, and sulphide are produced. V. H. Veley found that sulphur dioxide reacts with calcium oxide at 400°, forming much free sulphur which was attributed to a reaction with calcium sulphide and sulphur dioxide. D. L. Hammick observed only traces of sulphur are formed with fresh lime at incipient redness, and dried sulphur dioxide; the sulphite is formed as the primary product, and this is quickly converted to sulphide and sulphate. I. Guareschi found that the gas is absorbed by **soda-lime.** W. T. Smith and R. B. Parkhurst determined the solubility of sulphur dioxide in water, milk of lime, and milk of **magnesia** from 5° to 60° and 760 mm. The conc. of sulphur dioxide as sulphurous acid is proportional to its partial press. C. F. Wittich studied the action of sulphur dioxide on heated magnesia and found that the temp., 325°, at which absorption occurs, is also the temp. of decomposition of magnesium sulphite. D. L. Hammick, and G. Keppeler observed that **cupric oxide** reacts with sulphur dioxide before visible redness with the evolution of light and heat. The brick-red mass which is formed is a mixture of cuprous oxide and cupric sulphate: $3CuO+SO_2=Cu_2O+CuSO_4$, showing that the sulphur dioxide is oxidized, An acid sulphate may also be formed. D. L. Hammick also found that **mercuric oxide** acts as an oxidizing agent when heated in sulphur dioxide, forming mercuric and mercurous sulphates, free mercury, and sulphur trioxide: $4HgO+2SO_2=2Hg+2HgSO_4$; and $4HgSO_4+3SO_2=2Hg+Hg_2SO_4+6SO_3$. J. Meyer found that mercuric oxide, suspended in water, does not form a dithionate when it reacts with sulphur dioxide—*vide infra,* dithionic acid. According to D. L. Hammick, while **stannic oxide** is not attacked at a red-heat, **stannous oxide** reacts with incandescence, forming clouds of sulphur and traces of sulphur trioxide. The primary reaction is $18SnO+7SO_2=16SnO_2+2SnS+5S$; which is followed by $SnS+3SnO_2=4SnO+SO_2$, and the stannous oxide then reacts as before. When **lead oxide** is heated in the gas just below visible redness, a dull glow travels through the mass. No sulphur or sulphur trioxide was formed, but a black powder—a mixture of lead sulphide and sulphate—was produced: $8PbO+8SO_2=2PbS+6PbSO_4$. These possibly interact in the well-known way. J. Meyer observed that when sulphur dioxide is passed through water with **lead dioxide** in suspension, there is no perceptible change. F. Wöhler observed that lead dioxide in sulphur dioxide becomes incandescent, and lead sulphate is produced, and E. J. Russell and N. Smith found that a mixture of sulphur dioxide and oxygen gives lead sulphate. D. L. Hammick found that the **bismuth oxides** act as oxidizing agents on sulphur dioxide—bismuth monoxide gives a reddish-brown sublimate which may be bismuth trioxide, and a basic sulphate is produced; bismuth trioxide forms a black powder which contains a basic sulphate mixed with bismuth monoxide and free bismuth or both oxide and bismuth. No sulphide or free sulphur was formed, and only traces of sulphur trioxide. The main reaction is: $7Bi_2O_3+3SO_2=6BiO+4Bi_2O_3.3SO_3$. M. Traube obtained sulphur trioxide and chromic oxide when **chromium trioxide** is heated to 180° in sulphur dioxide. G. Grather and T. Nagahama studied the reduction of dichromates by sodium sulphite. W. Wardlaw and N. D. Sylvester, and G. Edgar found that a sexivalent **molybdenum salt** is not reduced by sulphur dioxide if it be allowed to act for, say, 8 hrs. at 90°, provided over $2{\cdot}5N\text{-}H_2SO_4$ be present and 2·5 grms. of MoO_3 per litre. W. Wardlaw and N. D. Sylvester found that tervalent molybdenum in sulphuric acid soln. is oxidized by sulphur dioxide to a stage between ter- and quinque-valent molybdenum while sulphur and molybdenum sulphide are precipitated. The degree of oxidation increases with increasing conc., and reaches a maximum approximating $Mo_2O_{4{\cdot}2}$. The reaction is probably reversible: $Mo_2(SO_4)_3+SO_2+2H_2SO_4 \rightleftharpoons Mo_2(SO_4)_5+S+2H_2O$, but the reduction of sulphuric acid soln. of molybdenum of higher valency to this stage does not occur, but the reaction $Mo_2O_5.nMoO_3+nH_2O+6HCl \rightleftharpoons 2MoOCl_3+3H_2O+nH_2MoO_4$ is reversible. In soln. corresponding to a stage just above the quinquevalent, sexavalent, and quinquevalent molybdenum are present, and, in accord with the above equilibrium, they will form molybdenum-blue in greater or smaller amount, depending on the acid conc. Molybdenum-blue is insoluble in 34 per cent. sulphuric acid, but in 56 per cent. acid it dissolves, giving rise to a yellow soln., whilst with 85 per cent. acid a green soln. is obtained. In acid of high conc. yellow, and green soln. are produced when sulphur dioxide reacts at 90° with molybdenum soln. at a slightly higher stage of oxidation than the quinquevalent. These effects are produced not by a specific action of the sulphur dioxide, but by the establishment of the above equilibrium relationship. Soln. of tervalent molybdenum salts in $\frac{1}{2}N$-H_2SO_4 react differently with sulphur dioxide, probably forming tetrathionic acid. D. L. Hammick observed that when **manganous oxide** is heated in sulphur dioxide, there is a dull red glow; sulphur and sulphur trioxide are produced and a green powder of manganese sulphide and sulphate with traces of higher manganese oxides is formed. At a dull red-heat, sulphur trioxide, but no free sulphur, is produced and manganese sulphate is formed. The main reaction is symbolized: $7MnO+10SO_2=MnS+6MnSO_4+SO_3+2S$; one secondary reaction is: $MnS+5MnSO_4=2Mn_3O_4+6SO_2$. E. J. Russell and N. Smith showed that dry **manganese dioxide** does not absorb dry sulphur dioxide; but D. L. Hammick showed that if the dioxide is finely divided and at a dull red-heat, interaction occurs with the evolution of light and heat, leaving a reddish-brown mixture of manganese sulphate and the two oxides Mn_2O_3 and Mn_3O_4: possibly the reactions are $MnO_2+SO_2=MnSO_4$; $2MnO_2+SO_2=SO_3+Mn_2O_3$; $3Mn_2O_3+SO_2=2Mn_3O_4+SO_3$; $Mn_3O_4+SO_2=2MnO+MnSO_4$; etc. J. Meyer found that when suspended in water, manganese dioxide forms sulphate, sulphite, and dithionate: $2MnO_2+4H_2SO_3=Mn_2(SO_3)_3+3H_2O+H_2SO_4$; $Mn_2(SO_3)_3=MnSO_3+MnS_2O_6$, and $MnSO_3+O=MnSO_4$. T. S. Dymond and F. Hughes observed that while manganese dioxide, suspended in water, oxidizes sulphur dioxide to sulphuric and dithionic acids, manganese tetratrioxide gives only sulphuric acid. J. Meyer and W. Schramm said that with manganese dioxide suspended in water there are two reactions: $2MnO_2+4SO_2=Mn_2(SO_3)_3+SO_3=MnSO_4+SO_2+MnS_2O_2$, and $MnO_2+SO_2=MnSO_4$; while with **manganic hydroxide** suspended in water, manganic sulphite is formed, as before, and this decomposes: $Mn_2(SO_3)_3=MnSO_3+MnS_2O_2$, and $Mn_2(SO_3)_3=MnSO_4+SO_2+MnSO_3$. There is no reduction to manganous salts, nor any decomposition of the manganic salt into manganous salt and dioxide. G. Keppeler observed that between 500° and 800° **ferric oxide** reacts slowly with sulphur dioxide: $3Fe_2O_3+SO_2=2Fe_3O_4+SO_3$. D. L. Hammick obtained a similar result, and he observed no reaction between ferrosic oxide and sulphur dioxide at dull redness; there is, however, a reaction with ferrous oxide. According to J. Meyer, **ferric, cobaltic, or nickelic hydroxide,** and **ruthenium tetroxide** form sulphites and dithionates; while sulphates are produced by the action of **sodium, barium, or magnesium dioxide** on sulphur dioxide. A. Rosenheim and E. A. Sasserath found that when a soln. of **perosmic acid** in soda-lye is treated with sulphur dioxide, sodium sulphonosmate is produced.

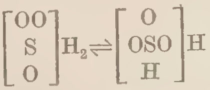
Sodium chloride, azide and sulphite, potassium cyanide and cyanate, ammonium chloride and sulphate; hydrazine sulphate, mercuric cyanide, cadmium chloride, and cupric sulphate are very sparingly soluble or insoluble in liquid sulphur dioxide; potassium chloride, bromide, and azide, lead iodide, and silver azide are sparingly soluble; and sodium iodide, potassium iodide, and thiocyanate, ammonium bromide, iodide, azide and thiocyanate are very soluble. A. Benrath and K. Ruland[32] found that **ceric sulphate** oxidizes sulphurous acid to eq. amounts of sulphuric and dithionic acids. J. A. Smythe and W. Wardlaw observed no evidence of oxidation, analogous to the case of stannous chloride, by the action of sulphur dioxide on **lead and thallium chlorides.** On the other hand, **cuprous chloride** is slightly oxidized, forming sulphur and cuprous sulphide; J. B. Firth and J. Higson studied the reaction with cupric chloride: $2CuCl_2+SO_2+2H_2O=Cu_2Cl_2+H_2SO_4+2HCl$.

W. Wardlaw, and W. Wardlaw and F. W. Pinkard represented the oxidation of cuprous chloride by sulphur dioxide in the presence of conc. hydrochloric acid by the equation: $2Cu_2Cl_2+SO_2+4HCl=4CuCl_2+2H_2O+S$. The reaction is probably reversible, but the reversibility is obscured by the reaction: $6CuCl_2+S+4H_2O=3Cu_2Cl_2+6HCl+H_2SO_4$. There is probably also a secondary reaction, forming black cuprous sulphide: $S+2Cu_2Cl_2=2CuCl_2+Cu_2S$. The degree of oxidation of the cuprous chloride is dependent on the initial conc. of the cuprous chloride; oxidation does not occur in soln. containing less than 30 c.c. of free hydrochloric acid (33 per cent.) in 250 c.c. of soln. at 95°; and if more than 150 c.c. of the hydrochloric acid is used, sulphur is precipitated. Soln. containing between 112 and 150 c.c. of the conc. acid furnish a precipitate of sulphur and cuprous sulphide; and with 38 to 112 c.c. of acid, the precipitate is cuprous sulphide alone. As the conc. of the acid decreases, the degree of oxidation is lowered, and even when black cuprous sulphide is precipitated, the degree of oxidation is small. W. M. Mebane and co-workers examined the solubility of **calcium phosphate** in aq. soln. of sulphur dioxide.

J. A. Smythe and W. Wardlaw found that **chromous and molybdous chlorides** are readily oxidized by sulphur dioxide to higher chlorides with the formation of hydrogen sulphide. The reduction of **mercuric chloride** by sulphur dioxide was noticed by A. Vogel, and F. Wöhler. F. Sartorius recognized the importance of the initial conc. of the mercuric chloride, and showed that the reduction is quantitative with a soln. of the chloride (1 : 80), sat. with sulphur dioxide after prolonged digestion at 70°–80°. P. A. Bolley obtained similar results. A. Sander said that the reduction of mercuric chloride by sulphurous acid: $H_2SO_3+2HgCl_2+H_2O=H_2SO_4+2HgCl+2HCl$, is quantitative only when the soln. contains not more than 2 grms. of sulphur dioxide per litre; with greater concentrations, sulphur dioxide escapes unoxidized from the boiling soln., with an excess of mercuric chloride and a cold soln. of sodium hydrosulphite, $2NaHSO_3+2HgCl_2=2HgCl(NaSO_3)+2HCl$; with sulphurous acid in place of the hydrosulphite, 2 mols of sodium hydroxide are needed to neutralize the reaction mixture for every mol of sulphurous acid, so that sodium hydrosulphite is first formed. If the neutralized soln. is boiled, it becomes acidic: $2HgCl(NaSO_3)+H_2O=2HgCl+Na_2SO_4+H_2SO_3$; and $H_2SO_3+2HgCl_2+H_2O=H_2SO_4+2HgCl+2HCl$. Normal sodium sulphite behaves like the hydrosulphite. J. A. Smythe and W. Wardlaw represented the reaction: $SO_2+4HCl+2Hg_2Cl_2=4HgCl_2+2H_2O+S$. L. M. Stewart and W. Wardlaw showed that this reaction applies when the hydrochloric acid present is $8N$- to $2N$-. With a decreasing conc. of hydrochloric acid, the amount of oxidation decreases, and at last, mercurous chloride is reduced: $Hg_2Cl_2\rightleftharpoons Hg+HgCl_2$, but not by the sulphur dioxide. The reduction of **mercurous chloride** by sulphur dioxide can take place in two ways: $Hg_2Cl_2+SO_2+2H_2O=2Hg+2HCl+H_2SO_4$; and $2HgCl_2+SO_2+2H_2O=Hg_2Cl_2+2HCl+H_2SO_4$ produce sulphuric acid in both cases. A. Vogel thought that mercurous chloride is converted by sulphur dioxide into a grey subchloride, but L. M. Stewart and W. Wardlaw observed that sulphur dioxide does not usually show a tendency to exert a reducing action in the presence of dil. hydrochloric acid; and they agree with E. Divers and T. Shimidzu, who found that:

> Ordinary calomel becomes a little greyish when suspended in a small quantity of water through which sulphur dioxide is passed . . . only traces of hydrochloric acid are found in the mother-liquor. We doubt if there is any reaction at all between either of the two, mercurous chloride and sulphurous acid, for when mercurous chloride is precipitated by sulphurous acid itself, it is of dazzling whiteness.

They also found that mercuric chloride dissolves more readily in aq. soln. of sulphur dioxide than in water alone, but not so in the presence of much sulphuric acid; and they suppose that in the reduction of mercuric chloride, the first stage results in the formation of mercuric hydrosulphite: $HgCl_2+2H_2SO_3=2HCl+Hg(HSO_3)_2$; and that this is partially hydrolyzed into mercurosic sulphite: $3Hg(HSO_3)_2+H_2O=Hg_3(SO_3)_2+H_2SO_4+3H_2SO_3$, which is then decomposed by the hydrochloric acid: $Hg_3(SO_3)_2+4HCl=HgCl_2+Hg_2Cl_2+2H_2SO_3$. The sulphuric acid formed by the reduction of the mercuric chloride prevents the remainder of the mercuric chloride from forming the essential intermediate hydrosulphite, and thus brings the reaction to a close. M. le Blanc and A. A. Noyes also observed that mercuric chloride and hydrochloric acid form a complex H_2HgCl_4. L. M. Stewart and W. Wardlaw showed that with a definite conc. of acid, the yield of mercurous salt is dependent on the conc. of the mercuric chloride present. If over 2·6 grms. per 120 c.c. of water are present at 95°, the reduction is incomplete after a 12 hrs.' digestion. Returning to the influence of the conc. of the hydrochloric acid, while oxidation occurs with $2N$- to $8N$-HCl; the mercurous chloride decomposes: $Hg_2Cl_2=Hg+HgCl_2$ with between $2N$- and $0·16N$-HCl; and the calomel is not affected by $0·16N$- to $0·0N$-HCl; there is a minute reduction: $Hg_2Cl_2+SO_2+2H_2O=2Hg+2HCl+H_2SO_4$ with $0·07N$- to $0·02N$-HCl, and this reduction increases with decreasing acid conc. down to neutrality—*vide* mercurous chloride—**4.** 31, 11—and mercuric chloride—**4.** 31, 12. O. Ruff observed that liquid sulphur dioxide and **aluminium chloride** in a sealed tube form **aluminium sulphurylchloride**, $AlCl_3.SO_2$, and the same compound is produced by the action of aluminium chloride on sulphuryl chloride (*q.v.*). P. Walden found that **ferric chloride** dissolves in liquid sulphur dioxide, forming a yellow soln. The reduction of ferric salts by sulphurous acid and sulphites was observed by R. Phillips, C. F. Schönbein, J. Meyer, H. J. Buignet, L. L. de Koninck, A. Vogel, P. T. Austen and G. B. Hurff, T. W. Hogg, R. W. Atkinson, B. Glasmann, A. C. Cumming and E. W. Hamilton, etc. J. A. Smythe and W. Wardlaw, W. Wardlaw, and W. Wardlaw and F. H. Clews studied the oxidation of **ferrous chloride** in acidic soln. by sulphur dioxide. The reaction: $4FeCl_2+SO_2+4HCl\rightleftharpoons4FeCl_3+2H_2O+S$ is reversible, but this fact is generally obscured by the reaction: $2FeCl_3+SO_2+2H_2O=2FeCl_2+2HCl+H_2SO_4$; but in the presence of conc. hydrochloric acid no sulphuric acid can be detected when ferrous chloride is oxidized by sulphur dioxide. Owing to the reversibility, only a limited yield is possible, and the degree of oxidation is dependent only on the initial conc. of the total iron. From the mass law, assuming that the active masses of acid, sulphur, and water are constant, the equilibrium condition is determined solely by the ratio of the ferrous to ferric iron. The most favourable temp. for the oxidation of ferrous chloride, in 33 per cent. hydrochloric acid, by sulphur dioxide is 95°; oxidation does not occur at 95° in soln. containing less than 165 grms. of free HCl per litre. A soln. of ferrous chloride in 22 per cent. hydrochloric acid gave a maximum yield of 8·6 per cent. of ferric iron when treated with a mixture of sulphur dioxide and hydrogen chloride containing 16 per cent. of sulphur dioxide; mixtures with 10–20 per cent. of sulphur dioxide give the best results under these conditions. Soln. containing 10–18·3 per cent. of ferric iron in 33 per cent. hydrochloric acid gave no evidence of oxidation or reduction; with more than this amount of ferric iron, reduction slowly occurred. The dependence of sulphur dioxide as an oxidizing agent on a high conc. of hydrochloric acid made it probable that hydrochloric acid and sulphur dioxide form a little thionyl chloride, and that the oxidizing properties of sulphur dioxide are really exercised through the medium of the thionyl chloride initially produced. Accepting the results of K. Schaefer, and of A. O. Rankine and C. J. Smith, *vide supra*, W. Wardlaw and N. D. Sylvester assume that the slowness of the reactions indicate that they are molecular and not ionic; that hydrated sulphur dioxide is formed $S<O_2+H_2O=HO.S.O.OH$; and that the peroxide group thus produced will give rise to an oxidizing reaction when in contact with a reducing agent; otherwise, it will assume the more stable configuration:



$$\left[\begin{matrix}OO\\S\\O\end{matrix}\right]H_2\rightleftharpoons\left[\begin{matrix}O\\OSO\\H\end{matrix}\right]H$$

Reactions with sulphur dioxide as an oxidizing agent can then be symbolized

$S<O_2+2H \rightarrow HO.S.OH$; $HO.O.S.OH+2H \rightarrow HO.S.OH+H_2O$. The initial reduction product of the sulphur dioxide and its hydrate is probably the hypothetical sulphyoxylic acid, which by further reactions can give rise to hyposulphurous or the thionic acids. When sulphur is precipitated as the result of an oxidation by sulphur dioxide, it may be considered as the end product of a series of unstable intermediate substances. According to O. C. Ralston, when sulphur dioxide, diluted with air is passed through a soln. of ferrous sulphate, the ferrous iron and the sulphur dioxide catalyze each other's oxidation, and the reaction : $2FeSO_4+SO_2+O_2=Fe_2(SO_4)_3$ occurs. The optimum temp. is 40°, and the best proportion of the two gases is about 7 per cent. SO_2 by vol. for crucibles about 1mm. diameter. The effect of press. is small. The presence of copper is detrimental to the reaction. Sulphur dioxide was found by W. Wardlaw and co-workers to have no reducing action on **ferric phosphate** dissolved in conc. phosphoric acid : but **ferrous phosphate** in conc. phosphoric acid is oxidized : $4Fe(H_2PO_4)_2+4H_3PO_4+SO_2=2H_2O+S+4Fe(H_2PO_4)_3$. It is believed that the reaction is really reversible, but is modified by the formation of complex stable compounds of ferric phosphate with phosphoric acid. S. R. Carter and J. A. V. Butler found that the speed of the reaction agrees with the assumption that an active reducing compound is produced by a primary reaction which is reversible, and by a second irreversible process this active substance decomposes with the formation of sulphur. The intermediate compound is probably not hydrogen sulphide ; hydrosulphurous acid and thiosulphuric acid have the necessary reducing qualities, but would not have a long enough life in strongly acid soln. An active form of sulphur could conceivably possess the required properties, and decompose into inactive sulphur at a rate required by the theory. J. Houben estimated ferrous and ferric iron together in acidic soln. on the assumption that when a ferric salt is reduced with sulphur dioxide, the increased acidity corresponds with two-thirds of the acid in combination with the ferric iron, $2FeCl_3+SO_2+2H_2O=FeSO_4+FeCl_2+4HCl$. J. Meyer observed that the reduction of a ferric salt most probably proceeds in stages ; thus, first, a red ferric ferrisulphite, $Fe[Fe(SO_3)_3]$, is formed, which slowly changes in the cold, more quickly on warming, into the ferrous salt, not, however, with the production of sulphuric acid, but dithionic acid, thus : $Fe[Fe(SO_3)_3]=FeS_2O_6+FeSO_3$. Before any increase in the acidity can take place, therefore, the dithionate must be decomposed, thus : $FeS_2O_6+H_2O=FeSO_4+H_2SO_3$, and it is not quite certain whether this is completed even by vigorous boiling. J. Pinnow found that a low acid conc. favours the interaction of a ferric salt and a sulphite ; quinone, quinol, and their respective sulphonic acids act as carrier-catalysts in the oxidation of a sulphite to sulphate by means of a ferric salt, and their effects increase with increase in the respective amounts present. In acid soln., their catalytic action is less pronounced. The increased yield of sulphate in the presence of quinone is not in accord with the suggestion of C. E. K. Mees and S. E. Sheppard that a dithionate is formed from quinone and a sulphite. The author finds that quinone is converted into its sulphonic acid. The regeneration of quinol or its sulphonic acids, by means of sulphurous acid, and its subsequent oxidation to quinone, can be effected only in acidic soln.

According to W. Wardlaw and co-workers, the facts that sulphur dioxide reduces most readily in a very dil. acid medium, and that it oxidizes most readily in a strong acid medium, may be explained on an ionic basis, oxidation being represented by the surrender of positive charges and reduction by the transference of negative charges. Sulphur dioxide in aq. soln. is generally regarded as a moderately weak and acid ionizing principally into $H^{\cdot}$-, $HSO_3{}'$-, and $SO_3{}''$-ions. It is in this condition that it reacts as a reducing agent. Thus : $2Fe^{\cdot\cdot\cdot}+SO_3{}''+H_2O=2Fe^{\cdot\cdot}+SO_4{}''+2H^{\cdot}$. In strongly acid soln. containing a large number of hydrions, the conc. of $SO_3{}''$-ions will be reduced, and, on the above assumption, its power of reducing should be diminished. This is in accordance with experimental results. Now let it be assumed that sulphur dioxide is capable of ionizing to an extremely minute extent as a base, yielding a correspondingly minute amount of sulphur ions. E. Fromm and G. Raiziss have shown that the sulphoxides, the organic analogues of sulphur dioxide have basic properties. This tendency will be all the greater, the larger the number of $H^{\cdot}$-ions present in soln. Thus, $H_2O+SO_2 \rightleftharpoons OS(OH)_2 \rightleftharpoons SO^{\cdot\cdot}+2OH'$; or $H_2O+SO^{\cdot\cdot} \rightleftharpoons S^{\cdot\cdot\cdot\cdot}+2OH'$. In view of the large number of hydrions present in the soln., the conc. of hydroxyl ions would be reduced to a very low value and the reaction towards the right favoured. Oxidation is now represented: $S^{\cdot\cdot\cdot\cdot}+4Fe^{\cdot\cdot} \rightarrow 4Fe^{\cdot\cdot\cdot}+S$. If oxidation takes place due to the ion-$SO^{\cdot\cdot}$, $2SO^{\cdot\cdot}+4Fe^{\cdot\cdot} \rightarrow 4Fe^{\cdot\cdot\cdot}+2SO$; $2SO+H_2O \rightarrow H_2S_2O_3$, which represents an intermediate stage in the reduction of sulphur dioxide to sulphur. Thiosulphuric acid would break up into sulphur dioxide and sulphur. This hypothesis is a modification of the thionyl chloride hypothesis of J. A. Smythe and W. Wardlaw.

According to W. R. E. Hodgkinson and J. Young, when dry sulphur dioxide acts on **chromates** or **dichromates,** there is a tendency to form chromium sulphate as well as the other metal sulphate, but in no case was the chromium sulphated to its fullest extent; the **permanganates** behave similarly. W. S. Hendrixson studied the reducing action of sulphurous acid on dichromates which is incomplete in acidic soln. owing to the formation of some dithionate. Alkaline soln. of sulphur dioxide were found by F. Heeren, L. P. de St. Gilles, M. J. Fordos and A. Gélis, and H. J. Buignet to be almost completely oxidized to sulphate; by permanganate; but in acidic soln., about one-fifth is oxidized to dithionate. I. M. Kolthoff said that the reaction is completed only in alkaline soln. with a large excess of permanganate; in acidic or neutral soln. the reaction was not complete in 24 hrs. even with a large excess of permanganate. This was attributed by W. S. Hendrixson to the formation of some dithionate. G. Lunge and J. H. Smith found that only 86 per cent. of sulphur dioxide is transformed into sulphuric acid. When sulphurous acid is dropped into a soln. of potassium permanganate there is a loss owing to the volatilization of the dioxide; T. S. Dymond and F. Hughes said that the loss is due to the formation of dithionic acid: $17H_2SO_3+6KMnO_4=2K_2S_2O_6+K_2SO_4+6MnSO_4+6H_2SO_4+11H_2O$. If sulphurous acid be introduced into an excess of permanganate, sulphuric acid alone is produced. T. Pilter showed that basic **phosphates** insoluble in water are transformed by sulphurous acid, under press. into acid phosphates. According to B. W. Gerland, sulphur dioxide converts **calcium orthophosphate** into **calcium sulphurylphosphate,** $Ca_3(PO_4)_2.SO_2.2H_2O$, while E. Rotondi observed that when calcium **magnesium orthophosphate** is heated with sulphurous acid, hydrophosphate and sulphite are produced; and with **barium or lead orthophosphate,** dihydrophosphate and sulphite are formed.

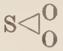
Some reactions of analytical interest.—When the sulphites are treated in the cold with dil. or conc. **sulphuric acid,** sulphur dioxide is given off recognizable by its odour. With **silver nitrate,** neutral sulphites or sulphurous acid gives a white precipitate of silver sulphite soluble in aq. ammonia, nitric acid, and in an excess of silver nitrate. When the latter soln. is boiled, a grey precipitate of silver is formed; and similarly when silver sulphite is boiled in water. O. Hackl[33] said that by means of silver nitrate it is possible to detect 0·001 grm. of SO_3'' as sulphite in 10 c.c. of water; or 0·00001 grm. of sulphur dioxide in 1 c.c. of water. No precipitation occurs with **barium chloride** in sulphurous acid, but with neutral sulphite soln., barium sulphite is precipitated. The precipitate is soluble in cold nitric acid, and when the soln. is boiled, insoluble barium sulphate is formed. If the sulphite contains sulphate, the precipitate with barium chloride may not be all soluble in the nitric acid. A similar precipitate is obtained with **strontium chloride,** but, as shown by W. Autenrieth and A. Windaus, thiosulphates do not give this precipitate. One part of calcium, strontium, or barium sulphite is soluble respectively in 800, 30,000, and 46,000 parts of water at 18°. White lead sulphite is precipitated by **lead salts.** The sulphites are oxidized to sulphates by **chlorine water.** The reducing action of sulphurous acid is shown by its decolorizing **iodine** soln., and acid **potassium permanganate** soln., **iodates, chromic acid,** soln. of **gold salts,** and **mercurous nitrate.** L. L. de Koninck observed that filter-paper soaked in potassium ferrocyanide and ferric chloride is coloured blue by sulphur dioxide or acid sulphites; and J. Persoz, that paper soaked in starch and potassium iodide soln. becomes blue when exposed to sulphur dioxide. At ordinary temp. **mercuric chloride** gives no precipitate with sulphurous acid, but when the soln. is boiled mercurous chloride is formed, and with an excess of sulphurous acid, the mercurous salt is blackened by forming mercury. According to A. Sander, when sodium salts of the following acids are treated with an excess of mercuric chloride, the reactions indicated in Table III occur. Polythionates and sulphites cannot exist together in a soln. **Nascent hydrogen** from zinc and sulphuric acid reduces sulphurous acid to hydrogen sulphide recognizable by its odour, and by its action on lead acetate. According to C. H. D. Bödeker, and K. A. Hofmann, if a neutral sulphite be treated with a dil. soln. of **sodium nitroprusside,** a faint pink colour is produced, but if an excess of zinc sulphate be added, the colour is red. If a little potassium ferrocyanide be present, the reaction is more sensitive, and, unlike thiosulphuric acid, sulphurous acid then gives a red precipitate. Neutral sulphites, not the hydrosulphites or free acid, rapidly decolorize dil. soln. of **fuchsine, malachite green,** and other triphenylmethane dyes. According to E. Votocek, soln. of thiosulphates or of di-, tri-, and tetrathionates do not decolorize these dyes; but soln. of mono- or poly-sulphides also remove the colour from the dye soln., and the sulphide ion must be removed by means of zinc or cadmium ions before the test with the dye is made. The best effects are obtained by using a mixture of 3 vols. of magenta soln. (0·25 grm. in 1 litre) and 1 vol. of malachite-green soln. of the same conc. The colour is restored on the addition of a small amount of acetaldehyde. If the original soln. is alkaline, carbon dioxide is passed in; if acid, an excess of sodium hydrogen carbonate is added. A soln. of 0·00006 grm. of sulphurous acid in 1 c.c. of water can readily be detected by this method. The reaction was studied by H. Leffmann and M. Trumper, and H. Fincke. The detection of thiosulphates, sulphites, sulphates, and sulphides has been discussed by R. G. Smith, W. P. Bloxam, etc.—*vide infra.*

TABLE III.—SOME REACTIONS OF THE SALTS OF THE OXYSULPHUR ACIDS.

Sodium salt.	Cold soln.	Reaction with methyl orange.	Boiling.	Reaction after boiling.
Sulphate . . .	No ppt.	Neutral	No change	Neutral
Sulphite . . .	No ppt.	Alkaline	Ppt.	Acid
Hydrosulphite . .	No ppt.	Acid	Ppt.	Acid
Sulphide . . .	Ppt.	Neutral	No change	Neutral
Thiosulphate . .	Ppt.	Acid	No change	Acid
Polythionate . .	Ppt.	Acid	No change	Acid

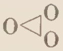
The constitution of sulphurous acid and the sulphites.—The empirical formula of a gaseous compound is based upon its percentage composition, and the atomic hypothesis; while the molecular formula, in addition, is coupled with Avogadro's hypothesis. After the empirical and molecular formulæ have been determined, the chemical properties of the compound are studied in order to trace the relations between the atoms of the molecules, and when this has been done for all the atoms in the molecule of the substance, the **constitution of the compound** is said to have been determined. The result of the investigation is expressed as a structural or graphic formula. "It is assumed," as W. Lossen [34] expressed it, "that the action of any particular atom on the other atoms in the molecule depends on the relative position of the atom in question; the properties and chemical behaviour of the molecule depend upon the actions of *all* the atoms on one another. Hence observations of the properties and the behaviour of a compound enable us to draw conclusions concerning the mutual actions of the atoms in the molecule of that substance, and the positions of the molecules relative to one another." A structural formula should summarize what is known about the chemical behaviour of the compound with respect to (i) the number and kind of atoms in the molecule; and (ii) the relations between the atoms in the molecule.

Several chemists have emphasized the formal analogy between sulphur dioxide and ozone; and although, like ozone, sulphur dioxide exhibits both oxidizing and reducing characters, the arguments in favour of the ozone structure:



$S\lhd\begin{matrix}O\\O\end{matrix}$

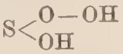
Sulphur dioxide.



$O\lhd\begin{matrix}O\\O\end{matrix}$

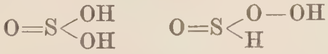
Ozone.

are not generally accepted. This formula for sulphur dioxide, however, was found by A. O. Rankine and C. J. Smith to agree better with the value calculated for the collision area (*q.v.*) than is the case with the formula $O{=}S{=}O$. The reducibility of sulphur dioxide by zinc and acid to the simple hydride, H_2S, does not prove that the sulphur atom is bivalent in sulphur dioxide; nor does the fact that the two atoms of oxygen in sulphuryl compounds are not replaceable by hydrogen, since the S-atom is fully saturated by two hydrogen atoms, and if oxygen atoms are affected, they are removed, not replaced, by the hydrogen. For instance, with ethyl chlorosulphonate, $C_2H_5(SO_2)Cl$, the two atoms of oxygen, on reduction, form water, and the chlorine is alone displaced by hydrogen, forming ethyl hydrosulphide, $C_2H_5.SH$, *i.e.*, ethyl mercaptan: $C_2H_5.SO_2.Cl+6H \rightarrow C_2H_5.SH+2H_2O+HCl$. The action of phosphorus pentachloride on sulphur dioxide, resulting in the formation of thionyl chloride, $SOCl_2$, is usually considered as establishing the constitutional formula $O{=}S{=}O$ for sulphur dioxide, and of $O{=}S{=}Cl_2$ for thionyl chloride. There are several possible methods of representing the constitution of sulphurous acid, and accordingly of the sulphites. The sulphur may be bi-, quadri-, or sexivalent:



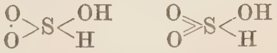
$S{<}\begin{matrix}O-OH\\OH\end{matrix}$

Sulphur dyad.



$O{=}S{<}\begin{matrix}OH\\OH\end{matrix} \qquad O{=}S{<}\begin{matrix}O-OH\\H\end{matrix}$

Sulphur tetrad.



$\begin{matrix}O\\ \dot{O}\end{matrix}{>}S{<}\begin{matrix}OH\\H\end{matrix} \qquad \begin{matrix}O\\O\end{matrix}{\gg}S{<}\begin{matrix}OH\\H\end{matrix}$

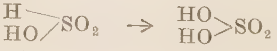
Sulphur hexad.

In one group of these formulæ, the hydrogen atoms are symmetrically placed with respect to the sulphur atom; and in the other group the hydrogen atoms are asymmetrical. The problem is to select from these graphic formulæ the one which best represents the orientation of the atoms in the molecule of sulphurous acid. W. Odling at first favoured the asymmetrical or sulphonic formula: $AgO.SO_2.Ag$, but later gave it up in favour of symmetrical, or dioxylic formula: $AgO.SO.OAg$. First, because the sulphites are in general less stable than the sulphonates; and second, because of the effect of phosphorus pentachloride and of phosphoryl chloride. The asymmetrical formula was favoured by A. Strecker, D. I. Mendeléeff, A. Michaelis and B. Landmann, W. Smith and T. Takamatsu, etc. In advocating the asymmetrical formula, E. Divers belittles the value of both arguments. J. K. Syrkin discussed the electronic structure.

The instability and ready oxidizability of the sulphites as compared with the sulphonates does not necessarily mean that these salts have a different constitutional formula. The ready oxidizability of the sulphites has been explained by the hypothesis that the basic radicle is attached directly to the sulphur atom of the SO_2-group, and that it is this basic radicle, not the central sulphur atom, which is oxidized. Similar remarks, according to H. Prinz, apply to the sulphurization of the sulphites from thiosulphates. In the more stable sulphonates, it is assumed that the hydrocarbon radicle is directly attached to the sulphur atom, and that it resists oxidation. The evidence is: (i) the oxidation of potassium ethyl sulphinate, $K(SO_2.C_2H_5)$, to potassium ethyl sulphonate, $KO(SO_2.C_2H_5)$, the sulphuryl group is probably unaffected, but the oxygen is interposed between the metal and sulphur. (ii) The sulphones—say ethyl sulphone, $(C_2H_5)_2SO_2$—have the same constitution as the sulphinates, and are not oxidizable because instead of a metal radicle being present, both the basic radicles are hydrocarbons, which resist oxidation. (iii) Ethyl sulphide, $(C_2H_5)_2S$, unlike the alkali sulphides say, Na_2S, does not oxidize in air, presumably because it is the presence of a metal united directly to sulphur which makes both the sulphides and sulphites oxidize in air. E. Divers explains the effect of moisture in facilitating the oxidation of sulphur dioxide by assuming that sulphurous acid—constituted $HO.SO_2.H$—is formed, and that the unoxidized hydrogen atom is readily attacked. The slow oxidation of sulphurous to dithionic acid, $H_2S_2O_6$, observed by V. A. Jacquelain, is similarly interpreted: $2(SO_2OH)H+O\rightarrow(SO_2OH)_2+H_2O$. When the radicle is not oxidizable, as is the case during the oxidation of silver sulphite, Ag_2SO_3, the instability of the salt is explained in a different manner—*viz.* the metal is more stable when free than when united as an oxy-compound.

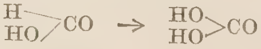
The argument that the sulphites contain two hydroxyl groups is also based on the extension to inorganic compounds of J. B. A. Dumas and E. Péligot's and A. Cahours' investigations on the action of phosphorus pentachloride on organic acids, etc., whereby each supposed hydroxyl group is replaced by equivalent chlorine atoms. Phosphorus pentachloride reacts with the sulphites forming thionyl chloride, $SOCl_2$, and hence it is argued that the sulphites have the equivalent of two hydroxyl groups. E. Divers holds that the thionyl chloride is here the result of a secondary reaction, and that the inference is invalid. This argument follows from Carius' observations that ethyl chlorosulphonate, $(C_2H_5)ClSO_2$, is the first product of the action of phosphorus pentachloride on sodium ethylsulphonate, $NaO(C_2H_5)(SO_2)$; and this compound decomposes slowly and spontaneously into sulphur dioxide and chloroethane, C_2H_5Cl; the sulphur dioxide then reacts with the phosphorus pentachloride, forming thionyl chloride. Accordingly, the formation of thionyl chloride by the action of phosphorus pentachloride on the sulphites is not conclusive evidence of their constitution because an unstable metal chlorosulphonate, say $NaClSO_2$, may be momentarily formed, to decompose immediately into the metal chloride and sulphur dioxide, which latter is acted upon by phosphorus pentachloride to form thionyl chloride. Phosphorus pentachloride is too drastic a reagent, and attacks both hydroxylic and non-hydroxylic radicles, and it is not therefore so satisfactory a test for the constitution of an acid as is obtained by the action of phosphorus oxychloride on the sodium salts, since this reagent employed by L. Chiozza does not confound the two kinds of radicles except in special cases, where at high temp. it is probably decomposed into the pentachloride and pentoxide: $5POCl_3=P_2O_5+3PCl_5$. This appears to be the case in the action of phosphorus oxychloride on boron oxide which was shown by G. Gustavson to furnish boron chloride and a product formed by the union of phosphorus pentoxide and boron trioxide. However, phosphorus oxychloride has little if any action on the dry sulphites—sodium, calcium, and lead. E. Divers represented the reaction: $POCl_3+3Na(NaO)SO_2=3NaCl+3SO_2+(NaO)_3PO$. At a higher temp., the products of the decomposition of the phosphorus oxychloride—P_2O_5 and PCl_5—react with the sulphite: $6CaSO_3+2P_2O_5\rightarrow2Ca_3(PO_4)_2+6SO_2$, followed by H. Schiff's reaction: $SO_2+PCl_5=SOCl_2+POCl_3$, so that three-fifths of the original phosphorus oxychloride is regained. In spite of the formation of thionyl chloride during the reaction between phosphorus oxychloride and the sulphites, the presence of two hydroxyl groups cannot be established in this way.

It has been said that the sulphites are analogous to the carbonates in virtue of the formulæ $(HO)_2SO$ and $(HO)_2CO$, but the ready oxidation of the one and not of the other suggests a different constitution unless it be remembered that sulphur can pass from a quadri- to a sexi-valent state while carbon cannot; it has been claimed further that the asymmetric sulphites are analogous to the formates, and that the sulphuryl SO_2-radicle in the one is analogous with the carbonyl CO-radicle of the other, and that when oxidation occurs, it is the hydrogen attached to the sulphuryl and carbonyl radicles respectively, which is oxidized:



$$\begin{matrix}H\\HO\end{matrix}\!\!>SO_2 \rightarrow \begin{matrix}HO\\HO\end{matrix}\!\!>SO_2$$

Sulphite. Sulphate.



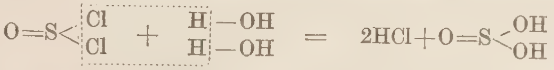
$$\begin{matrix}H\\HO\end{matrix}\!\!>CO \rightarrow \begin{matrix}HO\\HO\end{matrix}\!\!>CO$$

Formate. Carbonate.

so that the carbon analogy reacts between sulphites and formates, and between sulphates and carbonates; and the same analogy has been extended to the dithionates, $(SO_2.OH)_2$, and oxalates, $(CO.OH)_2$.

E. Divers also quoted the observations of R. Otto, and W. Spring on the reduction of the alkali di- and tri-thionates, and thiosulphate by sodium; E. Divers and T. Haga's observations on the reduction of nitrosylsulphonate by sodium; and W. Spring's observations on the action of sulphur dichloride and iodine on sulphites in support of the asymmetrical formula. This formula was also favoured by H. Baubigny, and H. Debus, and G. C. Stokes found that a salt with a monoxylic bond does not form a strongly fluorescing salt with quinine, but even quenches the fluorescence produced by an oxylic salt. E. Divers showed that a soln. of a sulphite or of sulphurous acid at once destroys the fluorescence of quinine, and, so far as the test is trustworthy, this indicates the presence of a monoxylic group.

On the other hand, the mode of formation of thionyl chloride, $O:S:Cl_2$, from sulphur dioxide, indicates that there is probably no change in the valency of quadrivalent sulphur when one of the oxygen atoms of sulphur dioxide is replaced by two chlorine atoms, and that each of the oxygen and chlorine atoms is directly attached to the sulphur. Like other acid chlorides, thionyl chloride is decomposed by water or alkaline soln., forming sulphurous and hydrochloric acids:

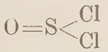


$$O{=}S{<}\begin{matrix}Cl\\Cl\end{matrix} + \begin{matrix}H-OH\\H-OH\end{matrix} = 2HCl + O{=}S{<}\begin{matrix}OH\\OH\end{matrix}$$

The reaction is interpreted to mean that sulphurous acid has a similar constitution to thionyl chloride; the two chlorine atoms of the last-named compound have been replaced by two hydroxyl groups derived from the water. Hence, it is inferred that the two hydroxyl groups of sulphurous acid are directly united with the sulphur atom. Otherwise expressed:

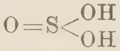
$O{=}S{=}O$

Sulphur dioxide.



$$O{=}S{<}\begin{matrix}Cl\\Cl\end{matrix}$$

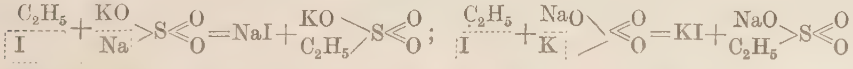
Thionyl chloride.



$$O{=}S{<}\begin{matrix}OH\\OH\end{matrix}$$

Sulphurous acid.

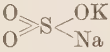
It is commonly assumed that *when an atom or group of atoms in a compound is replaced by another atom or group of atoms, the latter occupies the position vacated by the former without any essential structural change in the arrangement of the other atoms.* This rule does not mean that the relations subsisting between the atoms of the molecule are not altered during the replacement of one atomic group by another, for the hydrogen atoms in, say, C_2H_3OCl may be more or less easily affected by certain reagents than the hydrogen atoms in, say, C_2H_3OBr. The rule of the constancy of structural arrangement, and the action of water on thionyl chloride, make it probable that the two chlorine atoms of thionyl chloride are directly replaced by two hydroxyl groups. By neutralizing potassium hydrosulphite with sodium hydroxide or carbonate, and by neutralizing sodium hydrosulphite with potassium hydroxide or carbonate, two soln. are obtained from each of which crystalline potassium sodium sulphite can be separated. A. H. Röhrig, and H. Schwicker believed that the crystals prepared by these two different processes are different. Both products yield compounds with identical properties when the double sulphites are treated with methyl or ethyl iodide in a sealed tube. Assume, for the moment, that the reactions can be represented:

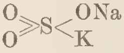


$$\begin{matrix}C_2H_5\\I\end{matrix} + \begin{matrix}KO\\Na\end{matrix}{>}S{\ll}\begin{matrix}O\\O\end{matrix} = NaI + \begin{matrix}KO\\C_2H_5\end{matrix}{>}S{\ll}\begin{matrix}O\\O\end{matrix}; \quad \begin{matrix}C_2H_5\\I\end{matrix} + \begin{matrix}NaO\\K\end{matrix}{>}S{\ll}\begin{matrix}O\\O\end{matrix} = KI + \begin{matrix}NaO\\C_2H_5\end{matrix}{>}S{\ll}\begin{matrix}O\\O\end{matrix}$$

where the metal directly united to the sulphur atom is alone replaced by the ethyl radicle. Sodium ethyl sulphonate and potassium iodide form the complex salt $4(C_2H_5.SO_2.ONa).KI$; and potassium ethyl sulphonate and sodium iodide, the complex salt $4(C_2H_5.SO_2.OK).NaI$, both of which were reported by H. Schwicker.

He also said that when the isomeric sulphites are boiled with ammonium sulphide, they are converted into isomeric thiosulphates (*q.v.*)—sodium ethyl sulphonate yielding sodium ethyl thiosulphate, $(C_2H_5)NaS_2O_3.H_2O$; and potassium ethyl sulphonate, potassium ethyl thiosulphate, $(C_2H_5)KS_2O_3$. These statements have not been established. K. Barth did obtain different products, but the evidence is not decisive. It is doubtful if different isomeric potassium sodium sulphites could exist in aq. soln., even if they were to exist in the solid state ; because, according to A. P. Sabanéeff, the reaction: $C_2H_5.SO_2.ONa+KI \rightleftharpoons C_2H_5.SO_2.OK+NaI$, would probably be reversible. G. S. Fraps, also, could find no difference in the products obtained by H. Schwicker's reactions ; and he concluded that there is "no evidence of the existence of isomeric potassium sodium sulphites." Consequently, if two isomeric salts, say:


$$\begin{matrix}O\\O\end{matrix}\!\geqslant\! S \!<\!\begin{matrix}OK\\Na\end{matrix}$$

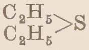

$$\begin{matrix}O\\O\end{matrix}\!\geqslant\! S \!<\!\begin{matrix}ONa\\K\end{matrix}$$

are capable of existing, the one in which the atom of potassium is directly connected with the sulphur atom is not stable and readily changes into the other. Otherwise expressed, there is at present no definite evidence of the existence of two different salts, $KO.SO_2.Na$ and $NaO.SO_2.K$; and hence it can be inferred that *the graphic formulæ of the sulphites correspond with two symmetrically placed hydroxyl groups in sulphurous acid,* and the formula is accordingly written: $HO-SO-OH$. G. Oddo discussed the constitution in the light of his theory of mesohydry. P. Pascal's magnetic observations favoured the $SO(OH)_2$ formula.

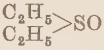
The rule of the constancy of structural arrangement might here easily lead us astray because the fact that no isomerism has hitherto been detected in the compounds prepared by the two different methods, may be due to the fact that with certain radicles only one configuration is stable and permanent. If another configuration be momentarily produced it immediately passes into the stable condition. Hence, the negative results obtained in the attempt to prepare two isomeric potassium sodium sulphites do not prove conclusively that an unsymmetrical sulphurous acid is non-existent, although the negative results may prove that there is only one stable or favoured configuration of $NaKSO_3$ or of $C_2H_5KSO_3$ under the conditions of the experiment.

Sulphurous acid, built up from quadrivalent sulphur, is a meta-acid—**metasulphurous acid,** $(HO)_2SO$, derived from **orthosulphurous acid,** $S(OH)_4$, by the loss of a mol. of water. The ortho-acid has not been prepared, but M. M. Richter obtained a number of derivatives—*e.g.* triphenyl chloro-orthosulphite, $S(OC_6H_5)_3Cl$; ethyl triphenylorthosulphite, $(C_6H_5O)_3S(OC_2H_5)$; etc.

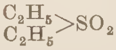
When ethyl sulphide, $(C_2H_5)_2S$, is oxidized with nitric acid, both **ethyl sulphoxide,** $(C_2H_5)_2SO$—melting at 8°—and **ethyl sulphone,** $(C_2H_5)_2SO_2$—melting at 72°—are formed:


$$\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!>\!S$$

Ethyl sulphide.

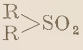

$$\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!>\!SO$$

Ethyl sulphoxide.

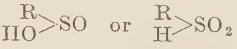

$$\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!>\!SO_2$$

Ethyl sulphone.

On the other hand, diethyl sulphoxide, $(C_2H_5)_2SO$, is readily reduced to the sulphide, showing that the oxidation is not likely to have affected the alkyl groups, but has confined itself to the sulphur atom. Ethyl sulphone has neither acidic nor basic properties ; 100 parts of water at 16° dissolve about 15·6 parts of the compound. The mode of formation of the alkyl sulphides, sulphoxides and sulphones, is supposed to show that both the hydrocarbon radicles are linked directly with the sulphur. The sulphones are remarkably stable, and cannot be readily reduced back to the sulphides. **Sulphoxylic acid,** S_2SO_2, is unknown, but the sulphones can be regarded as derivatives of an acid of this composition with both the hydrogen atoms directly united with the sulphur atom ; whereas the so-called **sulphinic acids** are derivatives of an acid of the same composition, but with one hydroxylic oxygen and one univalent hydrocarbon radicle, R, attached directly to the sulphur atom:

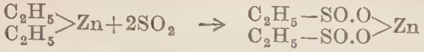

$$\begin{matrix}R\\R\end{matrix}\!>\!SO_2$$

Alkyl sulphone.


$$\begin{matrix}R\\HO\end{matrix}\!>\!SO \text{ or } \begin{matrix}R\\H\end{matrix}\!>\!SO_2$$

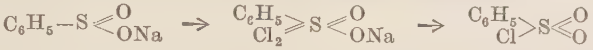
Alkylsulphinic acid.

The alkyl sulphinic acids, $R.SO.OH$, are usually liquids which rapidly oxidize to sulphonic acids, $R.SO_2.OH$, on exposure to air ; and, unlike the isomeric sulphones, they are oxidized by potassium permanganate and acetic acid to sulphonic ethers, $R.SO_2.OR$. The action of zinc ethide, $(C_2H_5)_2Zn$, on sulphur dioxide furnishes **zinc ethylsulphinate**, $(C_2H_5.SO.O)_2Zn$:



$$\begin{matrix}C_2H_5\\C_2H_5\end{matrix}{>}Zn+2SO_2 \rightarrow \begin{matrix}C_2H_5-SO.O\\C_2H_5-SO.O\end{matrix}{>}Zn$$

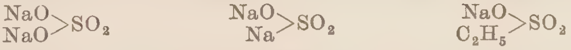
The transformation of **benzenesulphinic acid**, $C_6H_5.SO.OH$, into benzenesulphonic chlorides, $C_6H_5.SO.Cl$ (sulphur quadrivalent), by the action of phosphorus pentachloride, seems at first sight to exclude the formula $C_6H_5.SO_2.H$ (sulphur hexavalent), for benzene sulphinic acid, unless a consecutive series of reactions of this kind occurs :



$$C_6H_5-S{<}\begin{matrix}O\\ONa\end{matrix} \rightarrow \begin{matrix}C_6H_5\\Cl_2\end{matrix}{\geqslant}S{<}\begin{matrix}O\\ONa\end{matrix} \rightarrow \begin{matrix}C_6H_5\\Cl\end{matrix}{>}S{\leqslant}\begin{matrix}O\\O\end{matrix}$$

When ethyl mercaptan, $C_2H_5.SH$, is treated with nitric acid, it is oxidized to a derivative of sulphurous acid, **ethyl sulphonic acid**, $C_2H_5.SO_2.OH$, discovered by C. Löwig. Organic chemists consider that the alkyl radicle is directly united with the sulphur because of its mode of preparation, and also because it can be reduced back to mercaptan, $C_2H_5.SH$, by zinc and hydrochloric acid : $C_2H_5.S.H+O_2=C_2H_5.SO.OH$. The presence of a hydroxyl group in ethylsulphonic acid is inferred because it yields **ethylsulphonic chloride**, $C_2H_5.SO_2.Cl$, when heated with phosphorus pentachloride ; and ethylsulphonic chloride re-forms ethylsulphonic acid when hydrolyzed. The sulphonic acids contain the univalent SO_2OH-group with the sulphur atom directly united with a hydrocarbon radicle. In illustration, **phenylsulphonic acid**, or *benzenesulphonic acid*, $C_6H_5.SO_2.OH$, is formed by the action of conc. sulphuric acid on benzene, C_6H_6, thus $C_6H_6+HO.SO_2.OH \rightarrow C_6H_5.SO_2.OH+H_2O$; and hence, it is concluded that the residue SO_2OH of the sulphonic acids is the residue of sulphuric acid. This is further confirmed by the formation of chlorosulphonic acid, $Cl.SO_2.OH$, from sulphuric acid, and the re-formation of sulphuric acid when chlorosulphonic acid is hydrolyzed ; and by the formation of benzene sulphonic acid from chlorosulphonic acid and benzene : $Cl.SO_2.OH+C_6H_6 \rightarrow C_6H_5.SO_2.OH+HCl$.

When the sulphonic esters are fused with the alkali hydroxides, the corresponding alkali sulphite and alcohol is formed : $C_2H_5.SO_2.OC_2H_5+KOH \rightarrow K_2SO_3+C_2H_5.OH$; it is not likely that the alkali here deoxidizes the sulphuryl or SO_2-group to a thionyl or SO-group, and accordingly it is inferred that the alkali sulphite contains the SO_2-group, and has the formula $KO.SO_2.K$. In A. Strecker's and W. von Hemilian's reactions a sulphite is converted into a sulphonate, and this is interpreted : $(NH_4O.SO_2)NH_4+C_6H_5Cl \rightarrow (NH_4O.SO_2)C_6H_5+NH_4Cl$, for it is thought unlikely that phenyl chloride, C_6H_5Cl, can oxidize a SO-group into a SO_2-group. According to H. E. Armstrong and A. K. Miller, the benzenesulphonates can be hydrolyzed to sulphates : $C_6H_5.HSO_3+H_2O \rightarrow C_6H_5.H+H_2SO_4$; and since some of the sulphites can be similarly hydrolyzed to sulphates : $Ag_2SO_3+H_2O \rightarrow 2Ag+H_2SO_4$, it is suggested that the sulphates, sulphites, and sulphonates all contain the radicle SO_2.

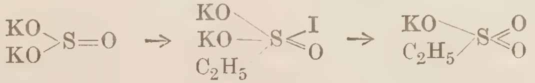


$$\begin{matrix}NaO\\NaO\end{matrix}{>}SO_2 \qquad \begin{matrix}NaO\\Na\end{matrix}{>}SO_2 \qquad \begin{matrix}NaO\\C_2H_5\end{matrix}{>}SO_2$$

Sulphate. Sulphite. Sulphonate.

There is probably a similar relation between the sulphinates and sulphites as that between the sulphites and sulphates, for R. Otto and H. Ostrop found that sodium benzene sulphinate, $C_6H_5.SO_2.Na$, reacts with sodium hydroxide at 250°–300°, forming sodium sulphite and benzene, a reaction which E. Divers interprets : $C_6H_5.SO_2.Na+NaOH \rightarrow C_6H_5.H+NaO.SO_2.Na$, and he argued that the constitution of the sulphinate cannot be $C_6H_5.SO.ONa$ because of the formation of $C_6H_5.SO_2.Cl$ when treated with phosphorus pentachloride. The subject was discussed by W. Strecker and P. Spitaler.

If sulphurous acid has the structure $(HO)_2SO$, it might be expected that the alkyl sulphonic acids obtained by treating the sulphites with the alkyl iodides would have an analogous formula. This is probably not the case. Silver sulphite with ethyl iodide form ethyl ethylsulphonate which on hydrolysis forms ethylsulphonic acid analogous with the acid obtained by the hydrolysis of mercaptan. Accordingly, it has been argued that the sulphites are salts of an unsymmetrical sulphurous acid, *viz.*, $HO.SO_2.H$. It is possible, however, that the formation of, say, potassium ethyl sulphonate, $C_2H_5.SO_2.OK$, from, say, a symmetrical potassium sulphite, $(KO)_2SO$, by the action of ethyl iodide, C_2H_5I, is due to the passage of quadrivalent sulphur in the sulphites to hexavalent sulphur in the sulphonic acids :

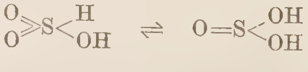


Sulphite. Intermediate addition product. Sulphonate.

As shown by A. Michaelis, C. W. Blomstrand, G. A. Barbaglia, W. Sarow, and W. A. Dixon, there is unimpeachable evidence of the existence of symmetrical and asymmetrical ethyl sulphites. **Symmetrical ethyl sulphite,** $(C_2H_5O)_2SO$, is a liquid of sp. gr. 1·1063(0°), boiling between 150° and 158·5° (760 mm.), and it is a salt of the symmetrical sulphurous acid because it is formed by the action of alcohol on thionyl chloride, $SOCl_2$, or sulphur chloride, SCl_2; the isomeric **unsymmetrical ethyl sulphonate,** $C_2H_5.SO_2.OC_2H_5$, is a liquid with a sp. gr. 1·1712(0°), and boiling between 213° and 214°. On hydrolysis with alkali (saponification) the equivalent of only *one* ethyl group is removed per molecule of the unsymmetrical diethyl sulphite or ethyl ethylsulphonate: $C_2H_5.SO_2.OC_2H_5+KOH \rightarrow C_2H_5.SO_2.OK+C_2H_5OH$; whereas with symmetrical diethyl sulphite, *two* ethyl groups are displaced: $(C_2H_5O)_2SO+2KOH \rightarrow (KO)_2SO+2C_2H_5OH$. It is not unlikely that under certain conditions, and by the action of certain reagents, the position of a hydrogen atom in the molecule can change so that it behaves differently under one set of conditions from what it does under another set of conditions. As a result of the **roving or wandering of the hydrogen atom,** when the attempt is made to prepare a compound by a likely reaction, another substance different from that which is expected is obtained although its chemical composition is the same. The phenomenon appears an exception to the rule of the constancy of structural arrangement. As usual, the supposed phenomenon has been given a name, **tautomerism** (C. Laar)—from ταὐτό, the same; μέρος, a part—and also the alternative name, **desmotropism** (P. Jacobsen)—from δεμός, a bond; τρέπειν, to change. *A substance is said to be tautomeric or desmotropic when it can react with other substances in such a way that it appears to be a compound with different constitutional formulæ.*

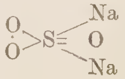
N. Bland and J. F. Thorpe propose to restrict the term *tautomerism* to those substances exhibiting the phenomenon under consideration where one individual is not stable enough to be isolated in a free state; and *desmotropism* to cases in which equilibrium mixtures of both forms are produced—which it may or may not be possible to isolate. Sulphurous acid may be an example of the former; and hydrogen sulphide of the latter. The term *structural isomerism* is applied to cases where both isomers are stable so that they can be isolated and do not form equilibrium mixtures at ordinary temperatures. The terms are commonly employed in a general sense without any implication as to the particular type of desmotropism.

In any given system, the two desmotropic modifications of a substance are in a state of equilibrium which is so very sensitive to external influences that the one modification readily changes into the other. A desmotropic change is thus an intra-molecular phenomenon which lends itself to observation only under exceptional conditions. It may be supposed that the position of a hydrogen atom in the molecule of sulphurous acid is labile, not rigid, because it can take up two different positions with respect to the other atoms. The change in the position of the hydrogen atom is accompanied by a change in the character of the linkages. In the present case, we have possibly:



$$\begin{matrix}O\\O\end{matrix}\!\gg S<\begin{matrix}H\\OH\end{matrix} \rightleftharpoons O{=}S<\begin{matrix}OH\\OH\end{matrix}$$

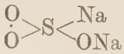
This hypothesis is employed by H. B. Rasmussen and S. Werner to explain anomalies in the rate of alkylation of sodium sulphite. F. Raschig represented the formulæ for sodium sulphite:



$$\begin{matrix}O\\O\end{matrix}\!>S\equiv\begin{matrix}Na\\O\\Na\end{matrix}$$

Normal sulphite.

and



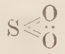
$$\begin{matrix}O\\O\end{matrix}\!>S<\begin{matrix}Na\\ONa\end{matrix}$$

Iso-sulphite.

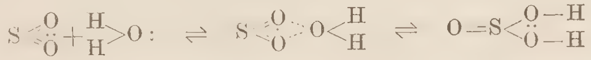
He said that the fact that the normal sulphites do not react with nitrites is explained by *die sterische Behinderung* or *steric hindrance*, meaning that owing to the central position of the sulphur atom in the molecule it is surrounded by other atoms so that it cannot take part in reactions which it otherwise would do were it not so masked. He said that the asymmetric formula is supported by the formation of amidosulphonate in the reaction: $NH_2OH.HCl+H.SO_2.ONa=H_2O+HCl+NH_2.SO_2.ONa$; at the same time, ammonium sulphate and nitrogen are formed. It is assumed that the sulphurous acid is mainly present in the tautomeric form $H_2 : SO_2 : O$, which, by replacement of the hydrogen atoms may form *diamidopersulphuric acid*, $(NH_2)_2SO_2 : O$, which oxidizes two mols of hydroxylamine yielding nitrogen and sulphamide: $(NH_2)_2SO_2 : O+2NH_2OH=N_2+3H_2O+(NH_2)_2SO_2$, and that the sulphamide decomposes into ammonia and amidosulphonic acid. He estimated that in an aq. soln. of sulphurous acid, two-thirds is present in the asymmetric form and one-third in the symmetric form. The difference of the two is shown by the reaction with chloroamide, which in the former case yields sodium chlorosulphonate, and in the latter case amidosulphonate.

The existence of two distinct series of sulphites does not necessarily mean that there are two different sulphurous acids, for there may be but one stable configuration of the acid itself under the conditions of the experiment. Evidence of slow and rapid changes in the arrangement of the atoms in a molecule is not wanting. The passage of ammonium cyanate, NH_4OCN, into urea, $CO(NH_2)_2$, is a trite example. There is a small difference in the refractive index and sp. gr. of ethyl acetoacetate when freshly distilled under diminished press. and after it has stood for some time: *e.g.* the refractive index (*C*-line) and sp. gr. of the freshly distilled compound are respectively 1·4165 and 1·0244; and after standing 20 hrs., these constants are respectively 1·4171 and 1·0247. This shows that some inter- or intra-molecular change takes place on standing.

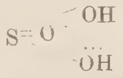
As indicated in connection with the optical properties of sulphurous acid, the work of C. S. Garrett showed that sulphurous acid may change in aq. soln. in accord with the scheme: $(n-1)H_2O+H_2SO_3 \rightleftharpoons SO_2.nH_2O$. J. A. N. Friend, using dots to represent what he calls latent valencies—**1**. 5, 14—and lines for free valencies, represented sulphur dioxide:


$$S{<}\begin{matrix}O\\ \ddot{O}\end{matrix}$$

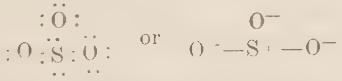
—*vide infra*, sulphur trioxide. The latent valencies here mutually saturate one another, and there is little tendency to form hydrates; the equilibrium condition with water is represented:


$$S{<}\begin{matrix}O\\ \ddot{O}\end{matrix}+\begin{matrix}H\\ H\end{matrix}{>}O: \rightleftharpoons S{<}\begin{matrix}O\\ O\end{matrix}{:}O{<}\begin{matrix}H\\ H\end{matrix} \rightleftharpoons O=S{<}\begin{matrix}O-H\\ \ddot{O}-H\end{matrix}$$

This accounts for the instability of the acid, and the fact that its soln. exhibits the properties of the dioxide. I. Smedley applies the theory of latent valencies by representing the constitution of sulphurous acid:


$$S=O\begin{matrix}OH\\ \vdots\\ \ddot{O}H\end{matrix}$$

H. Remy discussed the structure of sulphurous acid. According to J. J. Thomson, sulphur dioxide is an example of intramolecular ionization—*vide* **4**. 27, 4; and hyposulphurous acid. T. M. Lowry represented the sulphite radicle, SO_3'':


$$\begin{matrix}:\ddot{O}:\\ :O:\ddot{S}:\ddot{O}:\end{matrix} \quad \text{or} \quad \begin{matrix}O^-\\ O^-—S—O^-\end{matrix}$$

H. Burgarth also discussed the electronic structure. E. B. R. Prideaux gave for sulphurous acid:

$$\begin{matrix}HO\\ HO\end{matrix} S \quad O$$

The physiological action of sulphur dioxide.—F. C. Calvert[35] found that a soln. 1 : 1000 does not affect protoplasmic life or fungi. According to M. Ogata, sulphurous acid under all conditions is a powerful poison; a soln. with only 0·04 per cent. produced, after a few hours, a dyspnœa and darkening of the cuticle. The injurious action is mainly on the blood where the absorbed acid is converted into sulphuric acid. This action was not observed with sulphites. Diluted blood, decolorized with sulphur dioxide, shows no spectral absorption bands. H. Kionka found that relatively small proportions of sulphur dioxide in the atm. proved fatal. Doses of 0·02–0·04 grm. of sodium sulphite injected into frogs paralyze the heart, the central, and to some extent the peripheral nervous system. Dogs fed on the salt, or on food preserved by its use, suffer from injuries to various organs, especially the lungs and kidneys; there is local irritation of the stomach, and a fall of blood pressure, and hæmorrhages tend to occur. The use of the salt as a preservative is most reprehensible. L. Grünhut said that the comparative toxicity of sulphite soln. depends on the quantity of $[H_2SO_3]+[SO_2]$ contained therein. F. Franz and G. Sonntag found that sulphurous acid occurs in the urine after the administration of neutral sodium sulphite and formaldehyde, acetaldehyde sodium sulphite, and dextrose sodium sulphite. In men, as in dogs, by far the greatest part of the injected sulphite is oxidized to sulphate. In certain cases, after intervals of ten minutes or a quarter of an hour, sulphites can be detected in the urine. The quantity was, however, never more than 1 per cent. of the sulphite administered. According to J. König and J. Hasenbäumer, a carp weighing 195 grms. and a tench weighing 48 grms. were not injured by 17·5 mg. of calcium sulphite per litre; but 20–30 mg. of free acid and 30–50 mg. of calcium hydrosulphite are injurious. Goldfish are somewhat less sensitive. The trees in an atm. containing sulphur dioxide, as occurs, for instance, in the neighbourhood of smelting works, suffer severely. According to J. Schröder,[36] the coniferæ suffer more injury than ordinary foliaged trees. The number of stomata on the leaves bears no proportion to the amount of gas taken up. The sulphur dioxide disturbs the normal relation between absorption and transpiration of water, and the water taken up goes to the veins, and is not transmitted further. A decrease in the amount of the gas caused less disturbance in the amount of transpired water, though no simple proportion between the amount of the gas and of decrease was indicated. The amount of sulphur dioxide taken up by the leaves in the dark and with a lower temp. and moister air, is smaller and its injurious effects much less marked than in the light and with higher temp. and moister air; therefore the same amount of sulphur dioxide in the air is much less injurious to plants during the night than in the daytime. The amount of sulphur dioxide absorbed by pine-leaves is smaller than that absorbed by trees with ordinary foliage for equal surfaces, and as its effect on transpiration is less in the case of the pine, the cause of the greater injury to pine trees in nature must be due to the longer duration of the leaves, whereby the injury accumulates in them, whilst in trees with annual leaves the hurt to one year's foliage would have only an indirect influence on that of the following year. The alder, sycamore, ash, and especially maple, best withstand the action of smoke containing sulphur dioxide; next the pines suffer more than other trees, owing to the fact that, although their sensitiveness at first is less than that of other trees, their power of restoring lost leaves is much less. J. Stoklasa found that a small proportion of sulphur dioxide diminishes the carbon dioxide output of young pines; and the larger the proportion of sulphur dioxide the less the respiratory activity. The pine needles show a bleaching of the chloroplasts. According to J. König and J. Hasenbäumer, the presence of sulphurous acid and calcium hydrosulphite in soils increased the total ash of plants and the percentages of potassium, calcium, and sulphuric acid in the ash. The same effect has been observed when plants have been exposed to air containing sulphur dioxide. In water-cultures, 50 mg. of sulphurous acid or calcium hydrosulphite per litre killed the plants in a short time. According to A. Stöckhardt, in an atm. containing $\frac{1}{55,000}$ sulphur dioxide, the destruction of the chlorophyll-grains in wheat, oats, and peas, appears in a few hours; but, curiously, in a dilution of $\frac{1}{74,000}$, no injury takes place. Cabbages, and all plants having large strong leaves, are less affected. The fir tribe are far more susceptible to sulphur dioxide than deciduous trees; of the latter, white-thorn, beech, birch, and fruit trees are most affected; poplar, alder, and mountain-ash least. Wood smoke has no injurious effect on vegetation, but the smoke of coal and of some kinds of turf is very prejudicial; the injury is due to the sulphur dioxide produced on combustion. The leaves and twigs of trees poisoned by coal-smoke contain an abnormal amount of sulphuric acid. R. R. Tatlock and R. T. Thomson stated that the mere fact that sulphates occur in plants in excess of those grown in a pure atm. is no proof that any damage was caused to the plants by the acids of sulphur. They conclude that such damage can be assumed only if the percentage of SO_3 is considerably in excess of that normally present in the plants; and if, on wetting the surface of the plant with water and litmus, a leaf or other part of the plant shows an acid reaction. Yeast can be acclimatized to sulphur dioxide. According to G. Gimel, the adaption of yeast to sulphurous acid shows itself in its increased oxidizing power. A combination of sulphur dioxide with the yeast cells occurs since the percentage amount of sulphur in the ash of acclimatized yeast is greater than with ordinary yeast. The presence of potassium carbonate is favourable while that of calcium dihydrophosphate is not.

F. C. Calvert[37] found that the presence of $\frac{1}{1000}$th part of sulphurous acid with albumen prevented neither the production of protoplasmic life nor fungi. Sulphur dioxide has been compared with numerous other disinfectants, and it has been found that many disease germs resist its action for a long time—*e.g.* E. Baierlacher, T. Bokorny, T. Chiaromonte, H. Dubief and I. Brühl, V. Fatio, F. Hatton, G. Linnosier, A. Mehlhausen, A. L. A. Wernich, P. Miquel, F. Ravizza, H. Trembur, A. L. A. Wernich, and R. Wischin. The use of sulphur dioxide, and sulphites in the preservation of food-stuffs has been discussed by H. Schmidt, C. Grimaldi, and A. Kickton. M. Jacoby and H. Walbaum condemned the use of sulphites as food preservatives. The sulphurous acid is liberated in the organism—chiefly by the gastric acid, and it produces paralysis of the central nervous system. The presence of sulphur dioxide in sulphited, or sulphureted wines was discussed by A. Hubert, W. Kerp, J. Gautrelet, etc.

Some uses of sulphur dioxide.—The reducing properties of sulphur dioxide and of the sulphites are utilized in numerous chemical operations. It was recommended by R. Pictet[38] for the liquid of refrigerating machines. A large amount of sulphur dioxide is used for the manufacture of sulphuric acid, and for acid sodium or calcium sulphite required for the wood-pulp industry. Over half the wood used for paper-making is converted into pulp by the sulphite process. Sulphite soln. under press. and at a high temp., acts on the lignin and other incrustating matters breaking them down into products soluble in the sulphite-liquor. It is also used as an antichlor in paper bleaching. It is used in the textile industries as a bleaching agent for wool, and to a limited extent for cotton and silk; it is also used as a bleaching agent for straw, basket-ware, sponges, feathers, starch, etc. It is used for bleaching and dissolving the red phlobaphenes of tanning liquors and thus improves the colour of the leather—at the cost of the so-called solidity and weight of the leather. It is also used in the softening and deliming agents for hides and skins in tanneries. It is not employed so much as formerly as a disinfectant and antiseptic, thus it is employed in lotions for parasitic cutaneous affections, and in sanitary sciences as an after-fever fumigating agent; in combating vermin;[39] and as a preservative and anti-fermenting agent in the food-canning industry. It is used as an antiseptic and bleaching agent in the manufacture of glue, gelatine, etc. It is used in the rubber industry to prevent premature coagulating of the latex between the time the Hevea rubber tree is tapped, and the latex reaches the coagulating tanks in the factory. It also retards the action of oxidases present in the latex which would otherwise produce a discoloured rubber prone to tackiness. It is used for fumigating wine casks; and sulphur dioxide in any form is said to be advantageous in wine-making;[40] for sterilizing fermenting vessels and as a germicide in the brewery industry; there is an increased yield of glycerol and decreased yield of alcohol when sodium sulphite is present in a mixture of yeast and sugar, and the fact was for a time utilized in manufacturing glycerol. In the manufacture of sugar[41] for decolorizing and sterilizing crude sugar juices and glucose, sulphites and bisulphites act specifically in (i) preventing fermentation and forming colourless bodies which keep the juices in a state of reduction since oxidation products darken the colour of the cane-juices; (ii) coagulating and precipitating albuminous and gummy bodies not affected by heat; and (iii) assisting filtration. It is used in the preparation of aldehydes; perfumes, dyestuffs—*e.g.* for replacing the amido-groups of naphthylamines by hydroxy-groups; photographic developers for preventing the oxidation of the pyrogallol, hydroquinone, etc.; it is used directly in dyeing mainly because of its forming definite soluble compounds with the insoluble ketones—*e.g.* alizarine blue S, and alizarine green S. It is used as a stripping agent for dyed goods; in conducting sodium in some electroplating soln.; as a pickling agent in electroplating; and in the manufacture of hyposulphites, and thiosulphates.

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§ 16. The Alkali and Ammonium Sulphites

J. S. Muspratt[1] passed sulphur dioxide into conc. aq. ammonia until the ammoniacal smell had vanished; and added alcohol to the liquid. He thus obtained a mass of white crystals which had a feeble ammoniacal smell, and whose composition was represented by the formula $6NH_3.2SO_2.5H_2O$, or $(NH_4)_2SO_3.NH_4OH.H_2O$; neither J. C. G. de Marignac, nor A. Röhrig could obtain the *basic salt*—the product was the monohydrate of the normal salt. Anhydrous **ammonium sulphite**, $(NH_4)_2SO_3$, was prepared by R. de Forcrand, by heating the monohydrate for some hours at 130°–140° in a current of dry hydrogen; P. J. Hartog, by evaporating the aq. soln. by heat; and E. Divers and M. Ogawa, by keeping the monohydrate in a desiccator filled with ammonia gas over fused potassium hydroxide; and by heating dry ammonium thiosulphate in an atm. of hydrogen at 150°. The salt seems to sublime at 150°—presumably an effect of dissociation and recombination which E. Divers and M. Ogawa call *pseudo-sublimation*. A. F. de Fourcroy and L. N. Vauquelin passed sulphur dioxide through an aq. soln. of ammonia; combination occurred with a rise of temp. The soln. furnishes crystals of the *monohydrate*, which, according to J. C. G. de Marignac, are best obtained by cooling the liquid, or by precipitation with alcohol. A. Röhrig added that if the liquid be not cooled during the passage of the sulphur dioxide, the temp. may rise high enough to form the pyrosulphite. Some writers affirm and some deny that normal ammonium sulphite can be obtained by evaporation. E. Divers and M. Ogawa said that a conc. soln. of the salt, charged with ammonia, will deposit the normal sulphite on evaporation over potassium hydroxide at ordinary temp., and the moderately conc. soln. of ammonia, which must be used, has to be kept very cold while passing in the sulphur dioxide. If a dil. soln. of the salt be evaporated, most of the salt is decomposed. They recommended instead of evaporating the soln. to take advantage of its low solubility in the presence of such ammonia:

A soln. of ammonia of sp. gr. 0·895, containing 28 grms. NH_3 per 100 c.c. is treated with sulphur dioxide, while the containing flask is kept in motion in a mixture of ice and salt, the tube conveying the sulphur dioxide not dipping into the soln. The formation of a very little orange-coloured matter in the neck of the flask cannot be avoided, but this can be easily removed afterwards. When the soln. has become pasty from deposition of crystals of the salt, the passing of sulphur dioxide is stopped. Even at the common temp. the

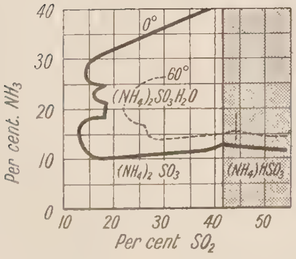


Fig. 55.—Solubility Curves of the System: NH_3–SO_2–H_2O at 0°. (The dotted line is the curve for 60°.)

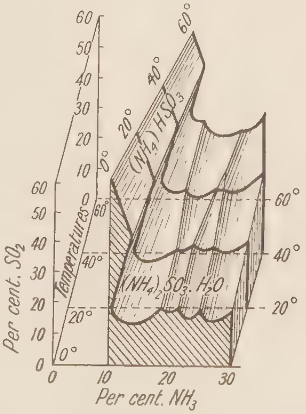


Fig. 56.—Equilibrium Conditions for the System: NH_3–SO_2–H_2O.

crystals do not sensibly dissolve in presence of the excess of ammonia. The salt, drained on a tile under close cover, can be dried either by filter-paper or by a short exposure in the desiccator over potassium hydroxide or carbonate, salted just before with ammonium chloride so as to maintain an atm. charged with ammonia. The product is eq. in quantity to about one-fourth of the ammonia taken.

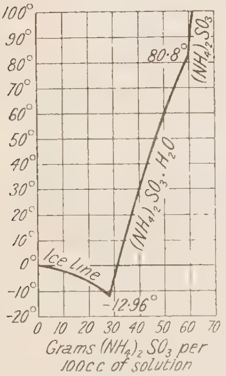


Fig. 57.—The Solubility of Ammonium Sulphite in Water.

P. de Lachomette passed an excess of sulphur dioxide into the ammonia, added more ammonia to convert the acid salt into the neutral salt and cooled the liquid for crystallization; while R. de Forcrand passed the sulphur dioxide into the conc. aq. ammonia until the soln. was nearly neutral, and then cooled the liquid—he said that the product is $(NH_4)_2SO_3.1\frac{1}{3}H_2O$. E. Terres and E. Hahn found that the salt is only the monohydrate. They made a partial study of the ternary system : NH_3–SO_2–H_2O. The curves at 0°, 20°, 40°, and 60° show a number of discontinuities, Figs. 55 and 56, which do not correspond with any perceptible change in the solid phase. The only solid phases in equilibrium with the soln. are the monohydrate, $(NH_4)_2SO_3.H_2O$, and the hydrosulphite, $(NH_4)HSO_3$, in the region of excess sulphur dioxide. A selection from the results is shown in Table IV, where concentrations are expressed in percentages. The results for the four temp. are plotted in Fig. 56. F. Ishikawa and H. Murooka measured the solubility of the salt between −13° and 100°. The transition point for $(NH_4)_2SO_3.H_2O \rightleftharpoons (NH_4)_2SO_3 + H_2O$ is 80·8°. The solubility data, expressed as S grms. of $(NH_4)_2SO_3$ in 100 c.c. of soln., are :

	−1·73°	−12·96°	−6·55°	0°	20°	50°	80°	90°	100°
S . .	4·691	28·855	30·62	32·40	37·80	47·26	58·89	60·00	60·44
Solid	Ice	$(NH_4)_2SO_3.H_2O$						$(NH_4)_2SO_3$	

The results are plotted in Fig. 57.

Table IV.—Isotherms of the System : NH_3–SO_2–H_2O.

Solid Phase.	0°				60°.			
	Solution.				Solution.			
	SO_2	NH_3	$(NH_4)_2SO_3$	Excess.	SO_2	NH_3	$(NH_4)_2SO_3$	Excess.
$(NH_2)_3SO_3.H_2O$.	17·47 27·19 41·78	9·66 10·74 13·44	32·93 36·63 45·83	0 6·99SO_2 16·50SO_2	27·60 34·15 44·16	15·21 15·40 16·61	50·07 52·52 56·64	0·53NH_3 5·18SO_2 12·92SO_2
2 solids . .	42·48	13·28	45·28	17·50SO_2	45·02	19·96	57·83	22·12SO_2
$(NH_4)HSO_3$.	46·68 49·70 53·46	12·66 12·42 11·48	43·17 42·35 39·14	22·87SO_2 26·34SO_2 31·87SO_2	46·99 53·29 56·27	16·38 15·90 14·86	55·87 54·22 50·67	16·19SO_2 23·12SO_2 28·32SO_2
$(NH_4)_2SO_3.H_2O$.	14·40 39·21 15·00	11·63 39·86 29·12	26·11 17·08 27·19	3·97NH_3 19·02NH_3 21·15NH^8	26·24 31·40 21·50	16·13 27·56 24·70	47·58 56·92 38·99	2·18NH_3 10·87NH_3 13·36NH_3

J. S. Muspratt passed ammonia and moist sulphur dioxide into absolute alcohol, and allowed the mixture to stand two days before drying the product between filter-paper. A. Röhrig passed the two gases into a soln. of alcohol and ether, and obtained the sulphite as a sandy powder. E. Scheitz observed that some sulphite is formed in the ammoniacal liquid of a gas-works by the oxidation of ammonium thiocyanate; and R. F. Carpenter and E. Linder observed that a little is found among the products of the reactions in Claus' kiln. In K. Burkheiser's process the ammoniacal gas from the gas-works, etc., is passed into acid ammonium sulphite soln. This salt is very soluble, and, as it is converted into the normal salt, $(NH)_4)_2SO_3.H_2O$ is precipitated. The process was discussed by E. Terres and E. Hahn. Patents on this subject were obtained by R. Laming, W. Marriott, W. C. Young, A. P. Price, A. McDougall, W. H. Deck, F. Wolf, P. Fritzsche, and J. and J. Addie.

Analyses of the salt in agreement with $(NH_4)_2SO_3.H_2O$ were made by J. S. Muspratt, J. C. G. de Marignac, A. H. Röhrig, and P. G. Hartog. According to J. C. G. de Marignac, and C. F. Rammelsberg, the tabular crystals of the monohydrate are monoclinic with the axial ratios $a:b:c=1·5276:1:0·7832$, and $\beta=97° 59'$, and, according to E. Terres and E. Hahn, the crystals appear in the habit of long thin needles of rhombic section. The sp. gr. at 25° is 1·4084 to 1·4124. F. Ishikawa and H. Murooka gave for the sp. gr. of some sat. aq. soln. at $\theta°/4°$:

	0°	10°	20°	30°	40°	50°	60°	70°	80°
Sp. gr. .	1·1792	1·1896	1·995	1·2097	1·2203	1·2306	1·2429	1·2558	1·2716

J. S. Muspratt said that the crystals are very deliquescent; J. C. G. de Marignac, that they are not so; while E. Divers and M. Ogawa found that the salt deliquesces in air owing to the fact that it evolves ammonia and becomes converted into the very deliquescent pyrosulphite. In a dry atm., the salt becomes anhydrous without losing ammonia. A. F. de Fourcroy and L. N. Vauquelin said that the salt has a fresh, pungent, and rather sulphurous taste, forming, according to E. Terres and E. Hahn, a white powder of the sulphate. According to R. de Forcrand, the heat of formation of the solid salt is $(S_{solid},3O_{gas},4H_{2gas},N_{2gas})=215·44$ Cals.; $(S_{gas},3O_{gas},4H_{2gas},N_{2gas})=218·00$ Cals.; $(SO_{2gas},2NH_{3gas},H_2O_{gas})=64·8$ Cals.; $(SO_{2soln.},2NH_4OH_{soln.})=25·4$ Cals.; $(NH_4HSO_{3soln.},NH_4OH_{soln.})=21·24$ Cals.; $\{2(NH_4)_2S,3O_2\}=301·2$ Cals.; $((NH_4)_2SO_{3solid},H_2O_{liquid})=3·82$ Cals.; and $((NH_4)_2SO_{3solid},H_2O_{solid})=3·39$ Cals. M. Berthelot gave $(2NH_{3soln.},H_2SO_3)=29·00$ Cals. For the heat of soln. of one part of the anhydrous sulphite in 60 parts of water at 8°, R. de Forcrand gave $-1·54$ Cals.; for the crystals $(NH_4)_2SO_3.1\frac{1}{3}H_2O$, $-5·36$ Cals.; P. J. Hartog gave for the monohydrate, $-4·34$ Cals. at 13°; and for the soln. of 3·567 grms. of the monohydrate in 4 litres of an eq. of hydrochloric acid, $-7·46$ Cals. R. de Forcrand gave for the heat of oxidation, $((NH_4)_2SO_3,O)=66·4$ Cals. If an excess of aq. ammonia be added to the aq. soln., $((NH_4)_2SO_{3soln.},NH_4OH_{soln.})=0·46$ Cal. G. Halphen observed that the electrolysis of the ammoniacal soln. furnishes the hyposulphite. According to A. F. de Fourcroy and L. N. Vauquelin, and J. S. Muspratt, the monohydrate volatilizes entirely when heated without forming sulphate, and during the action it evolves ammonia and water, and a sublimate of what is probably pyrosulphite. E. Divers and M. Ogawa found that when gradually heated in a slow current of nitrogen, at 90°, the salt becomes moist and ammonia escapes; and at 100°, both water and ammonia continue to escape for $2\frac{1}{2}$ hrs. When gradually heated to 120°, the monohydrate becomes converted one-third into the anhydrous salt, and one-third into pyrosulphite, by loss of water and ammonia; and then the nearly stable complex of these salts, with the other third of the original salt, becomes converted into the nearly anhydrous normal sulphite between 120° and 150°, sulphur dioxide and water escaping. The presence of water is essential to the occurrence of both changes; dry ammonium pyrosulphite partly sublimes as such at 150°, and partly changes into sulphate and trithionate. If heated more rapidly in an open tube, the results will be those obtained by J. S. Muspratt, for then water is more quickly expelled, and some pyrosulphite can be deposited as a sublimate. A. Bineau stated that at 134°, the salt blackens mercury without giving off gas. A. Miolatti and E. Mascetti measured the effect on the conductivity of progressive additions of 0·02N-alkali to sulphurous acid of such a strength that 5 c.c. of acid is completely neutralized by 33·5 c.c. of 0·02N-alkali with methyl orange as indicator. These results, illustrated in Fig. 58, agree with the existence of hydrosulphite and pyrosulphite. J. S. Muspratt said that the aq. soln. reacts alkaline; and J. S. Muspratt, J. C. G. de Marignac, and P. de Lachomette observed that the salt is slowly oxidized in air; P. J. Hartog, that the dry salt oxidizes more quickly than when moist; and R. de Forcrand thought that the alleged hydrate, $(NH_4)_2SO_3.1\frac{1}{3}H_2O$, is less oxidizable than the monohydrate. Probably the hydrate of R. de Forcrand is the imperfectly dried monohydrate. J. S. Stas said that the salt is stable in the presence of an excess of ammonia if oxygen be excluded. A. F. de Fourcroy and L. N. Vauquelin found that nitric acid converts the salt into ammonium nitrate and sulphite with the evolution of nitric oxide, and sulphur dioxide. At 12°, the salt dissolves in its own weight of water, and it is still more soluble in hot water; ammonia is evolved when the aq. soln. is boiled. H. Stamm studied the solubility of the salt in aq. ammonia, and found that soln. with 0·019, 1·468, and 3·530 mols. of NH_3 per 100 grms. of water dissolve respectively 0·500, 0·176, and 0·033 mol. of $(NH_4)_2SO_3$. E. Terres and E. Hahn found the percentage solubility of the salt in water to be 32·9, 36·5, 42·5, and 50·0 per cent. $(NH_4)_2SO_3$ respectively at 0°, 20°, 40°, and 60°. The partial press., p mm., of the soln., expressed in C grms. of $(NH_4)_2SO_3$ per 100 c.c. of soln., are:

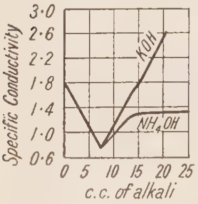


Fig. 58.—The Effect of the Progressive Addition of Alkali on the Conductivity of Sulphurous Acid.

20°	C	.	7·42	15 51	21·28	29·70	44·19
	p	Total	17·325	17·020	16·861	16·747	16·284
		SO_2	0·016	0·030	0·031	0·047	0·064
		NH_3	0·01	0·10	0·18	0·30	0·51
		H_2O	17·30	16·89	16·65	16·40	15·70
40°	C	.	10·53	19·12	26·51	35·13	45·78
	p	Total	54·739	55·274	55·708	56·349	56·728
		SO_2	0·009	0·024	0·038	0·059	0·098
		NH_3	0·54	1·15	2·06	3·08	3·88
		H_2O	54·19	54·10	53·61	53·21	52·75
60°	C	.	9·48	21·60	30·10	42·57	46·05
	p	Total	137·229	141·937	146·759	149·599	150·110
		SO_2	0·029	0·037	0·059	0·099	0·110
		NH_3	3·20	8·40	13·80	18·30	19·5
		H_2O	134·00	133·50	132·9	131·20	130·50

The results show that the partial press. of ammonia and of sulphur dioxide over soln. of ammonium sulphite are almost linear functions of the concentration; the values for ammonia are much higher than the corresponding values for sulphur dioxide, but both are sufficiently small, even at 40° and over conc. soln., to permit a practically quantitative removal of either constituent from a gas by washing. J. S. Muspratt said that the salt is slightly soluble in alcohol; and J. I. Pierre, that it is more soluble in alcohol than potassium sulphite. W. Eidmann, and A. Naumann found the salt to be insoluble in acetone; and A. Heynsius, that it precipitates egg-albumen completely from its soln. M. Prud'homme showed that zinc reduces ammonium sulphite to the hyposulphite. J. S. Stas observed that the salt separates iodine from ammonium iodide or from iodic acid, and in the last case some sulphur is formed. F. Ishikawa and H. Murooka observed no evidence of the formation of a chemical compound between ammonium sulphate and sulphite in aq. soln. between the eutectic point —21·5° and 100°. No solid soln. were observed.

W. Eidmann, and A. Naumann seem to have had the idea that **ammonium hydrosulphite,** NH_4HSO_3, can be obtained. E. Terres and E. Hahn obtained the solid under the conditions indicated in Figs. 55 and 56. The crystals are hexagonal prisms. They form a white powder of sulphate when exposed to air. The solubilities at 0°, 20°, 40°, and 60° are respectively 72·8, 74·5, 80·3, and 86·1 per cent. E. Terres and A. Heinsen represented the mutual solubilities of ammonium sulphate and sulphite by the curves, Fig. 59, and those of ammonium sulphate and hydrosulphite by the curves, Fig. 60. In the latter diagram, the dotted curves refer to soln. also saturated with sulphur dioxide. No complex salts are formed.

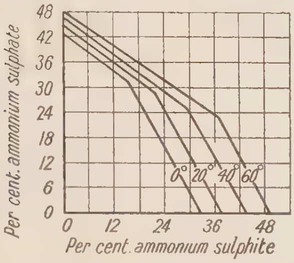


FIG. 59.—Mutual Solubilities of Ammonium Sulphate and Sulphite.

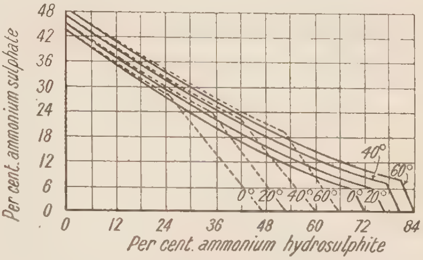


FIG. 60.—Mutual Solubilities of Ammonium Sulphate and Hydrosulphite.

E. Terres and A. Heinsen found that the speed of oxidation of soln. of ammonium sulphite or hydrosulphite is reduced with increasing concentration of the soln., and hence inferred that the oxidation process is mainly concerned with the ionized salt. The rate of oxidation of the hydrosulphite increases with a rise of temp. more quickly than is the case with the sulphite. A temp. of 40° to 50° was found to be most suited for the oxidation of the soln. The air oxidation of the hydrosulphite is catalyzed by lead dioxide, but no catalyst has yet been found to accelerate the air oxidation of the sulphite. If a denotes the barometric press. less the partial press. of the ammonia and sulphur dioxide, and x the monometric reading in the time t, then the speed of oxidation, with a constant mass of sulphite, corresponds with

$$k=\frac{1}{t}.\log\frac{a}{a-x}$$

The value of k decreases with a decrease in the conc. of the oxygen, and an increase in the conc. of the sulphite.

A. P. Sabanéeff and W. Speransky obtained silky needles of **hydrazine sulphite,** $(N_2H_4)_2H_2SO_3$, by neutralizing a soln. of the pyrosulphite with hydrazine hydrate, and evaporating the liquid in vacuo over sulphuric acid. F. Ephraim and H. Piotrowsky also obtained indications of the formation of a hydrazine sulphite by the action of hydrazine on thionyl chloride (*q.v.*).

A. Röhrig passed sulphur dioxide into water with lithium carbonate in suspension, heat is developed and a yellow liquid is formed. Needle-like crystals of monohydrated **lithium sulphite,** $Li_2SO_3.H_2O$, are produced by evaporating the soln. on a water-bath, or over sulphuric acid. Alcohol precipitates a white, granular mass of the monohydrate.

J. A. N. Friend and D. W. Pounder obtained the anhydrous salt as a white powder by passing a mixture of sulphur dioxide and hydrogen into a cream of lithium carbonate and water until effervescence ceases. The product is then heated in a current of dry hydrogen at 180° to 200° until the anhydrous salt is formed. It melts with partial decomposition at 455°, and some lithium sulphide is formed in accord with A. Röhrig's equation: $4Li_2SO_3=3Li_2SO_4+Li_2S$. If alcohol or ether be added to a strongly acid soln., A. Röhrig said that the *dihydrate*, $Li_2SO_3.2H_2O$, is formed; but J. A. N. Friend and D. W. Pounder could not prepare the dihydrate. J. Danson had previously reported a *hexahydrate*, $Li_2SO_3.6H_2O$, to be precipitated by adding alcohol, or boiling the soln., but this has not been confirmed. No *lithium hydrosulphite*, $LiHSO_3$, has been obtained; but J. A. N. Friend and D. W. Pounder prepared some of its derivatives with acetone, acetaldehyde, and benzaldehyde. A. Röhrig reported soluble **lithium sodium sulphite,** $6Li_2SO_3.Na_2SO_3.8H_2O$; and **lithium potassium sulphite,** $LiKSO_3.\frac{1}{2}H_2O$.

L. Coniglio[2] found traces of alkali sulphites in the products of the normal activity of Vesuvius. A. F. de Fourcroy and L. N. Vauquelin prepared **sodium sulphite,** Na_2SO_3, by passing sulphur dioxide through a soln. of sodium carbonate until the carbon dioxide is driven off, and evaporating the soln. out of contact with air. C. F. Rammelsberg saturated a soln. of sodium carbonate with sulphur dioxide, added to that an equal amount of sodium carbonate, and evaporated the liquid for crystallization. S. L. Shenefield and co-workers prepared heptahydrated sodium sulphite free from sulphate by the following process:

> Carefully purified sulphur dioxide was passed into a soln. of sodium carbonate to saturation, the requisite amount of sodium carbonate was added to transform the resultant sodium hydrosulphite into the normal sulphate, and the soln. cooled to 0°, whereby a crystalline meal of the heptahydrate was obtained. All the operations should be carried out in the absence of oxygen and the damp crystals will be free from sulphate. The crystals oxidize when kept in an atm. free from oxygen; this is attributed to autoxidation.

According to C. Schultz-Sellack, the salt separates from strongly alkaline soln. at ordinary temp., and on warming a saturated neutral soln. M. Berthelot saturated a soln. of 100 grms. of sodium hydroxide, in 100 c.c. of air-free water, with sulphur dioxide, and then added 100 grms. of sodium hydroxide dissolved in as little water as possible. The soln. was evaporated in vacuo. P. J. Hartog used a similar process. E. Priwoznik converted a soln. of sodium thiosulphate into one of sodium sulphite by treating it with copper. R. Payelle and E. Sidler heated dry sodium hydrosulphite with the calculated quantity of the hydrocarbonate; G. Tauber heated sodium sulphite; and E. Dresel and J. Lenhoff passed an excess of ammonia under press. into a soln. of the calculated proportions of sodium chloride and ammonium sulphate, at 15°, and obtained anhydrous sodium sulphite as a precipitate; and J. Kranz by the action of sulphur dioxide on sodium fluoride and gelatinous silica: $6NaF+SiO_2+2SO_2=Na_2SiF_6+2Na_2SO_3$. H. Blumenberg treated borax with sulphur dioxide when boric acid is precipitated and sodium hydrosulphite is formed. The preparation of the commercial sulphite is described in E. Schütz, *Die Darstellung von Bisulfiten und Sulfiten* (Halle a. S., 1911).

E. Mitscherlich said that sodium sulphite dissolves copiously in water at 33°, and the solubility decreases with rise of temp., so that, as C. F. Rammelsberg observed, the soln. saturated in the cold deposits the salt when warmed. P. Kremers observed that 100 parts of water at 0° dissolve 14·1 parts of salt; at 20°, 25·8 parts; and at 40°, 49·5 parts, but his salt was not of a high degree of purity. A. F. de Fourcroy and L. N. Vauquelin gave 24·80 for the percentage solubility at 100°. Solubility determinations were made by H. B. Hartley and W. H. Barrett, N. B. Lewis and A. C. D. Rivett, D. L. Hammick and J. A. Currie, and by F. Förster and co-workers. Analyses of the salt deposited in the cold were made by A. F. de Fourcroy and L. N. Vauquelin, J. C. G. de Marignac, C. F. Rammelsberg, H. B. Hartley and W. H. Barrett, and A. H. Röhrig showed that the *heptahydrate*, $Na_2SO_3.7H_2O$, is produced. C. F. Rammelsberg's formula $Na_2SO_3.6H_2O$ should in all probability be $Na_2SO_3.7H_2O$. J. S. Muspratt reported the formation of a *decahydrate*, $Na_2SO_3.10H_2O$, said to be less soluble than decahydrated sodium carbonate. C. Schultz-Sellack, A. Röhrig, and H. B. Hartley and W. H. Barrett were unable to confirm the existence of the decahydrate although the observations of H. Traube on the solid soln. of decahydrated sodium sulphite and carbonate make it probable that the decahydrate can exist under exceptional circumstances. Expressing the solubility, *S*, in percentages, H. B. Hartley and W. H. Barrett obtained for the stable system :

	−3·5°	−2·77°	−0·76°	2°	5·9°	10·6°	21·6°	47°	60·40°	84°
S . .	11·11	4·04	2·1	12·91	14·98	16·68	21·91	21·96	22·05	22·04
Solid phase	Ice			$Na_2SO_3.7H_2O$				Na_2SO_3		

The ice-curve cuts the solubility curve at the eutectic −3·5°, and there is a transition temp. in the neighbourhood of 21·6° or 22·1°. The transformation is very sluggish since 0·8° above that temp. only 0·1 per cent. was changed in 20 hrs. The transition temp. was found by F. Förster and co-workers to be 33·4°, and they obtained for the solubilities in grams Na_2SO_3 per 100 grms. of soln. :

	−1·3°	0°	9·20°	19·90°	26·85°	33 10°	35·6°	46·0°	66·4°	97·0°
S . .	11·25	12·54	15·60	20·82	24·32	28·06	27·70	26·19	24·06	21·32
	$Na_2SO_3.7H_2O$						Na_2SO_3			

The eutectic temp. is −3·45°. The results are plotted in Fig. 61. H. B. Hartley and W. H. Barrett found that the conditions under which ice and salt separate spontaneously from supersaturated soln. are summarized by the lower curve of Fig. 61. There is a hypertectic point at about −9·2. In no case is there any evidence of the spontaneous crystallization of any hydrate other than $Na_2SO_3.7H_2O$. N. B. Lewis and A. C. D. Rivett gave 31·5° for the transition temp. ; H. B. Hartley and W. H. Barrett, 22° ; F. Förster and co-workers, 33·4° ; K. Arii, 33·6° ; and D. L. Hammick and J. A. Currie, between 25° and 32°. D. L. Hammick and J. A. Currie studied the ternary system : Na_2SO_3–NaOH–H_2O at 0·15°, 20°, 25°, and 32°. The results for the two extreme temp. are summarized in Figs. 62 and 63. At 0·15°, the solubility of the sulphite in presence of excess of sodium hydroxide is very small, and the co-existing solid phases are sodium sulphite heptahydrate, anhydrous sodium sulphite, and sodium hydroxide tetrahydrate. The isotherms at 20° and 25° are very similar except that sodium hydroxide monohydrate replaces the tetrahydrate. At 32°, however, the sodium sulphite heptahydrate is no longer formed, in agreement with the value 31·5° found by N. B. Lewis and A. C. D. Rivett for the transition temp. $Na_2SO_3.7HO \rightleftharpoons Na_2SO_3$, but con-

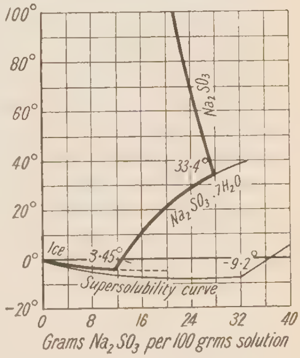


FIG. 61.—Solubility Curves of Sodium Sulphite.

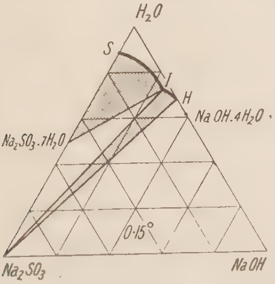


FIG. 62.—Equilibrium in the Ternary System : Na_2SO_3–NaOH–H_2O at 0·15°.

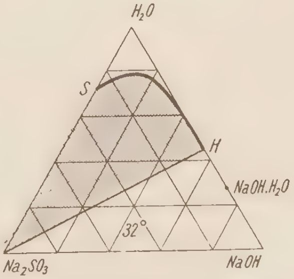


FIG. 63.—Equilibrium in the Ternary System : Na_2SO_3–NaOH–H_2O at 32°.

trary to the value 22° found by H. B. Hartley and W. H. Barrett. The discrepancies are possibly due to the existence of anhydrous sodium sulphite in more than one metastable phase; and to the fact that the low transition temp. of H. B. Hartley and W. H. Barrett refers to the most stable form of the anhydrous sulphite. In Fig. 62, soln. within *SI* are in equilibrium with the heptahydrate; and those within *IH* are in equilibrium with the anhydrous salt. The point *H* lies very close to the side H_2O—NaOH, which means that the solubility, of sodium sulphite in an excess of soda-lye, is very small. The point *H* represents soln. of the anhydrous sulphite in equilibrium with tetrahydrated sodium hydroxide. At 32°, heptahydrated sodium sulphite no longer appears. L. Wöhler and J. Dierksen found the mutual solubility of sodium sulphite and sulphate to be:

	23°	40°	60°	80°
Na_2SO_4 . .	9·55	18·48	14·21	14·95 per cent.
Na_2SO_3 . .	15·25	16·26	16·59	15·15 ,,

Observations were also made by N. B. Lewis and A. C. D. Rivett, who also found that anhydrous sodium sulphite and sulphate can form mixed crystals of varying stabilities, there being three, and possibily four, distinct metastable series at 25° and 37·5°. A study of the ternary system at temp. at which only anhydrous phases can exist is summarized in Figs. 65 and 66. There are 5 solubility curves, *A*, *B*, *C*, *D*, and *E* corresponding respectively with mixed crystals S_A, S_B, S_C, S_D, and S_E. The phase S_A is very short, indicating that the sulphite does not mix freely with the sulphate in soln. containing a high proportion of sulphate; with soln. above 10 per cent. of sulphite, there is a break and the phase S_B appears. The phase S_C is not extensive, but is greater at 40° than at 60°. S_D is metastable with respect to S_E; and the phase S_D is richer in sulphate than S_E.

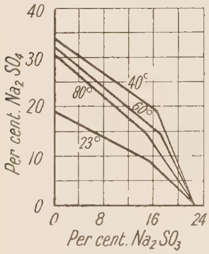
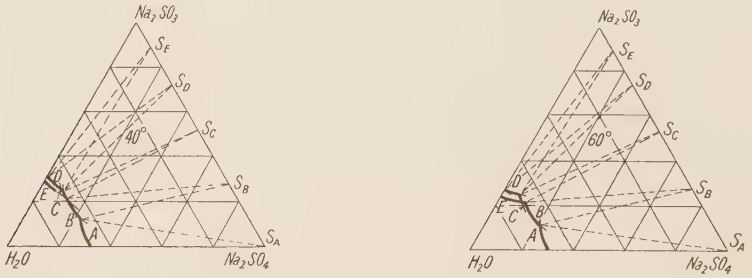


FIG. 64.—Mutual Solubility of Sodium Sulphite and Sulphate.

P. J. Hartog showed that the anhydrous salt furnishes short, hexagonal, prismatic **crystals,** which were found by H. B. Hartley and W. H. Barrett to be terminated by a basal plane and pyramidal faces; they are probably holohedral, with the axial ratio $a:c=1:1·1246$. The **cleavage** parallel to the basal plane is perfect. The crystals are strongly birefringent, and cleavage fragments show a uniaxial figure of negative character in convergent light. The crystals of the heptahydrate were shown by C. F. Rammelsberg, J. C. G. de Marignac, and A. des Cloizeaux to be monoclinic prisms with the axial ratios $a:b:c=1·5728:1:1·1694$, and $\beta=93°\ 36'$. H. Traube observed that this hydrate forms mixed crystals with heptahydrated sodium carbonate. H. B. Hartley and W. H. Barrett found the **specific gravity** of the anhydrous salt to be 2·6334 at 15·4°; and they gave 1·5939 for that of the heptahydrate at 15°. H. J. Buignet found 1·561 for the sp. gr. of the hydrated salt. H. G. Greenish and F. A. U. Smith



FIGS. 65 and 66.—The Ternary System: Na_2SO_3–Na_2SO_4–H_2O.

gave 1·21 for the sp. gr. of a soln. sat. at 15°. A. F. de Fourcroy and L. N. Vauquelin, and C. F. Rammelsberg observed that the hydrate loses water when heated below 150° without thereby melting; and at a higher temp., it melts to a yellowish-red mixture of a mol of sodium sulphide, and 3 mols of sulphate. H. Reck discussed the **efflorescence** of sodium sulphite. D. N. Tarassenkoff found that the percentage change in weight, δw, of the heptahydrate in an atm. with the press. of water vapour is p mm., at 15°:

p .	0·20	5·45	9·00	9·45	10·05	(22·7 per cent. H_2SO_4)
δw .	−49·58	−49·23	−5·85	+0·18	+0·53	+0·62

and with the anhydrous salt:

p .	9·00	9·2	9·7	10·05	22·7 per cent. H_2SO_4	
			28 days	38 days	3 days	66 days
δw .	0	0	+7·33	57·93	39·58	103·58

while the **vapour pressure,** p mm., of the heptahydrate is:

	0°	20°	30°	37°	40°	50°	60°	70°
p .	2·3	12·8	25	37	47	82	132	209

K. Arii measured the vap. press. of these systems, and found the transition temp. —heptahydrate to anhydride—to be 33·6°. He gave $\log p=10·65647-2797·12T^{-1}$ for the system $Na_2SO_3.7H_2O-Na_2SO_3$; $\log p=8·50733-2138·23T^{-1}$ for a sat. soln. and $Na_2SO_3.7H_2O$; and $\log p=9·04857-2304·20T^{-1}$ for Na_2SO_3 and a sat. soln. F. Förster and K. Kubel observed that the **thermal decomposition** of sodium sulphite at 600° may be represented: $4Na_2SO_3 \rightleftharpoons 3Na_2SO_4+Na_2S$; but above 900° the reaction $Na_2SO_3=Na_2O+SO_2$ disturbs the equilibrium. The equilibrium is not completed in 2 hrs. at 1200°. The rate of decomposition increases rapidly between 600° and 700°, but only slowly between 700° and 800°. M. Picon found that anhydrous sodium sulphite, in vacuo, at 700°, is rapidly converted into sulphate and sulphide: $4Na_2SO_3=3Na_2SO_4+Na_2S$. In air the anhydrous thiosulphate is stable at 100° for 15 days, but at 120° slow decomposition (complete in one month) into sulphate and sulphur dioxide occurs. Since the salt always contains traces of sulphur, the primary decomposition is probably into sulphur and the sulphite, atmospheric oxidation converting the latter into sulphate and sulphur dioxide: $Na_2S_2O_3+3O=SO_2+Na_2SO_4$. R. de Forcrand gave for the **heat of formation** (S,3O,2Na)=130·5 Cals.; $(SO_{2gas},Na_2O_{soln.})=45·75$ Cals.; SO_2 (64 grms. in 4 litres) and Na_2O (31 grms. in 2 litres) gave 30·56 Cals.; and $(NaHSO_{3soln.},Na_2O_{soln.})=13·92$ Cals., while J. Thomsen gave 13·1 Cals. R. de Forcrand gave for the **heat of solution** of the heptahydrate −5·55 Cals. at 10°, using a gram of the salt in 35 parts of water. P. J. Hartog gave for the heat of soln. of the anhydrous salt in 50 parts of water, 2·71 Cals. at 18°. V. J. Sihvonen found maxima in the **reflection ultra-red spectrum** at 10·6μ and 19·5μ. K. Barth found that the **electrical conductivity** of aq. soln. agrees with the assumption that the salt furnishes 3 ions: $Na_2SO_3 \rightleftharpoons 2Na^{\cdot}+SO_3''$; and for the molecular conductivity at 25°, he gave for a mol of the salt in v litres of water:

v .	0·25	0·5	1·0	2·0	4·0	8·0	16·0	32·0	64·0	256	1024
μ .	27·5	39·6	50·6	60·1	68·4	75·0	82·3	89·0	95·0	103·8	107·5

Sodium sulphite has a fresh taste, which afterwards appears sulphurous; and it turns red litmus blue. J. Obermiller measured the hygroscopicity of the salt. The anhydrous salt is stable in dry **air**: and A. Lumière and A. Seyewetz said that it is not changed in air at 100°, but in moist air it is rapidly oxidized at 15°. The aq. soln. oxidizes more readily the less its concentration so that with a 20 per cent. soln. the **rate of oxidation** is negligibly small. S. L. Bigelow also noticed that the curves representing the conc. of the soln. with time are straight lines until a conc.

of $0{\cdot}002N$-Na_2SO_3 is attained when they rapidly bend downwards, indicating a marked decrease in the speed of oxidation. This is explained by assuming that the velocity constant of the reaction is large, so that until the conc. of the soln. is small, oxygen is removed from the soln. faster than it is absorbed. He also found that small quantities of organic compounds—mannitol, alcohols, glycerol, aldehydes, ketones, and ethers—act as negative catalysts in slackening speed of the oxidation; oxalic acid has very little effect. E. Saillard found that the oxidation of sulphites to sulphates is retarded in sucrose soln., the amount of retardation being the greater the greater the conc. of the sucrose. Rise in temp. increases the velocity of change. Invert sugar has approximately the same effect as sucrose. Nitrogenous substances, for example, asparagine, aspartic acid, glutamic acid, and potassium lactate, also exert a retarding action, whilst sodium chloride has no effect. S. W. Young observed the retarding influence of alkaloids; and H. S. Taylor, of *iso*propyl, secondary *iso*butyl, and benzyl alcohols. The subject was studied by W. P. Jorissen. A. and L. Lumière and A. Seyewetz applied the term anti-oxidizing agents to those substances—negative catalysts—which retard the rate of oxidation of aq. soln. of sodium sulphite.

The following anti-oxidizing agents are arranged in order of decreasing activity: *quinol,* p-*aminophenol hydrochloride, glycine,* p-*phenylenediamine, catechol, metol, metaquinone, diaminophenol hydrochloride, adurol, edinol,* and *eikonogen. Acetone* behaves in the reverse way. The effect is independent of time, temperature, light, and the concentration both of the sulphite and the anti-oxidizing agent, but is diminished by the addition of alkaline substances, *acetone* or *formaldehyde.* The action appears to be catalytic in character. A soln. of sodium sulphite may be preserved for a prolonged period by the addition of a small quantity of one of the more active anti-oxidizing agents.

A. Titoff showed that the speed of oxidation is really very slow unless stimulated by the presence of a catalytic agent. Copper sulphate has a marked action and the effect is approximately proportional to the amount of catalyst present, less marked are the effects with silver nitrate, gold chloride, potassium dichromate, manganese and ferrous sulphates, and potassium chloroplatinate. The speed of oxidation is retarded by stannous and stannic chlorides, sodium nitrate, mannitol, potassium cyanide, and substances which form complexes with copper salts. The reaction is of the first order, and is within the limits of experimental error, independent of the conc. of the oxygen. W. Reinders and S. I. Vlès confirmed the results of A. Titoff, and they showed that cupric and ferric ions exert a maximum catalytic activity when the $H^{\cdot}$-ion concentration is between $p_H=4$ and $p_H=12$. Nickel and cobalt ions are active only in alkaline soln. In ammoniacal soln., no oxidation occurs except in the presence of copper salts; the reaction is then unimolecular, and proportional to the conc. of the copper catalyst—the conc. of oxygen has very little influence on the result. F. O. Rice added that if the reaction with respect to sodium sulphite is unimolecular, the process requires the production of atomic oxygen or else it is either bimolecular with respect to sodium sulphite, or a heterogeneous reaction. He showed that if the air be thoroughly freed from dust, it is not affected by oxygen during several hours' action. Copper alone has no catalytic activity because the sulphite soln. may be freed from dust by precipitating in it copper hydroxide; the resulting clean soln. does not oxidize in the presence of oxygen. It is therefore inferred that the oxidation of sodium sulphite is a dust reaction, and that the walls of the containing glass vessel have a negligible effect. C. Moureau and co-workers studied the catalytic action of sulphur on the autoxidation of sodium sulphite. N. N. Mittra and N. R. Dhar found that the oxidation of sodium sulphite by atm. air as a primary reaction is accelerated in the presence of sodium nitrite, potassium oxalate, ferrous ammonium sulphate, sodium arsenite, manganous, cobaltous, or nickelous hydroxide, or sodium thiosulphate as secondary reaction. W. P. Jorissen and C. van den Pol found that sodium sulphite does not induce the oxidation of sodium oxalate and nitrite by air or oxygen under ordinary conditions; sodium sulphite does not induce the oxidation of the arsenite when the alkalinity of the soln. is too great. S. Miyamoto found that the presence of stannous hydroxide in alkaline soln. inhibits the oxidation of sodium sulphite in air. C. Moureau and C. Dufraisse found that the presence of many sulphur compounds accelerates the oxidation of sodium sulphite —*vide supra*, the oxidation of sulphur. E. Divers and T. Shimidzu agreed with the view that the sulphites are oxidized by a reaction:

$$\genfrac{}{}{0pt}{}{\mathrm{Na}}{\mathrm{NaO}}\!>\!SO_2+H_2O+O_2=\genfrac{}{}{0pt}{}{\mathrm{NaO}}{\mathrm{NaO}}\!>\!SO_2+H_2O_2$$

R. M. Purkayostha and N. R. Dhar said that the reaction is semi-molecular: $Na_2SO_3+O=Na_2SO_4$. T. Sabalitschka and G. Kubisch found that the solid deposit which separated in a bottle in which sodium hydrosulphite soln. had been stored consisted of crystalline sodium sulphate and a small quantity of free sulphur, whilst the dregs of the soln. contained sulphurous acid, sodium bisulphate, and sodium sulphate. E. Isnard found that when an old soln. of sodium hydrosulphite was added to a soln. of sodium thiosulphate, there was a precipitation of sulphur and a slight evolution of hydrogen sulphide as if a mineral acid had been added. The bottle containing the old soln. had a crystalline mass at the bottom, and on top of this a layer of sulphur, and the acidic liquor had a slight smell of sulphur dioxide. Presumably the hydrosulphite had been partially oxidized to sulphate and hydrosulphate; then followed the reaction $3NaHSO_3=Na_2SO_4+NaHSO_4+S+H_2O$; a little sodium sulphide is also formed and remains in a state of equilibrium in the acidic soln. When this soln. is added to sodium thiosulphate, sulphur is precipitated, and the sulphur dioxide reacts with sodium sulphide, liberating hydrogen sulphide: $3SO_2+2Na_2S+2H_2O=2Na_2SO_4+2H_2S+S$; or $2SO_2+2Na_2S+2H_2O=2Na_2SO_3+2H_2S$; or else $Na_2S_2O_3+2NaHSO_4+H_2O=H_2S+2NaHSO_4+Na_2SO_4$. The oxidation of sulphite soln. was also studied by S. Miyamoto.

According to E. H. Riesenfeld and T. F. Egidius, a neutral soln. of sodium sulphite reacts with **ozone**, forming sulphate and dithionate. A. Longi and L. Bonavia found **sodium dioxide** readily oxidizes the sulphites quantitatively to sulphates. F. Ferraboschi observed no ozone is formed by the oxidation of the sulphite with **hydrogen dioxide**—*vide supra*. J. H. C. Smith and H. A. Spoehr found that sodium ferropyrophosphate acts as a catalyst in the oxidation of soln. of sodium sulphite, and that an intermediate compound of oxygen with the catalyst is produced. According to J. Milbauer and J. Pazourek, the presence of cobalt sulphate in 0·01*M*- to 0·001*M*-soln. of sodium sulphite acts as a positive catalyst in accelerating the oxidation by air. Unlike S. L. Bigelow, and N. Schilow, they found that copper and manganese salts are not very active catalysts in conc. soln. of sulphites. In conc. soln. 0·5 molar, weak alkalinity of the medium intensifies the oxidation, if no precipitation of the catalyzing agent is caused. Strong alkalinity retards the reaction. An acid medium has a similar influence, the rapidity of the reaction increases with rising temp.

R. E. Liesegang found that paper soaked in a soln. of the sulphite is sensitive to **light**, and the illuminated part colours gallic acid, or silver nitrate brown; if the illuminated paper be kept in darkness for a long time, the browning no longer occurs. F. Thomas found that red light accelerates the oxidation of soln. of sodium sulphite, while the action is slower in yellow, green, and violet light than it is in darkness—it is slowest of all in violet light. O. Loew exposed sealed tubes containing dil. soln. of sulphates, sulphites, sulphurous acid, and sulphuric acid to sunlight, for 3 months, and found that while the sulphurous acid soln. remained clear for 2 months before it deposited sulphur and formed sulphuric acid, the other soln. were not changed. J. H. Mathews and co-workers found that sodium sulphite soln. are more rapidly oxidized in ultra-violet light than in ordinary light, and F. H. Getman added that light is an essential factor in the oxidation of hydrosulphite soln. The increased activity of ultra-violet light has been attributed to the formation of ozone or hydrogen dioxide, which is the actual oxidizing agent, since W. G. Chlopin found that ordinary moist air exposed for a few minutes to ultra-violet light contains traces of ozone, hydrogen dioxide, and nitrogen trioxide. The effect has also been attributed to the ionization of the oxygen by the ultra-violet light, but G. Bredig and W. Pemsel exposed oxygen to ultra-violet light, X-rays, uranium rays, and phosphorus one-fourth of a second before it was bubbled into a soln. of sodium sulphite, and found no increase in the speed of the reaction. R. B. Mason and J. H. Mathews observed that pure oxygen, and ozone greatly increase the rate of oxidation of aq. soln. of sodium sulphite in light and in darkness; and that the rate of oxidation is dependent on the rate at which the gas is bubbled through the soln., and on the character of the bubbles. J. H. Mathews and L. H. Dewey found that uranium salts accelerate the photochemical oxidation. Hydroquinone and phenol in $0{\cdot}001N$-soln. were found by R. B. Mason and J. H. Mathews to accelerate the reaction. J. H. Mathews and co-workers found that quinine sulphate, rubber, pyridine, glycerol, benzaldehyde, quinol, and methyl and ethyl acetates all act as negative catalysts. The action of quinol decreases as the action proceeds owing, presumably, to its decomposition by light. Copper sulphate and carbamide had no appreciable effect on the velocity of the photochemical oxidation of soln. of sodium sulphite. F. H. Getman also noted the retarding influence of sugar soln. R. B. Mason and J. H. Mathews could detect no relationship between the light absorption of the catalysts and their action on the photochemical oxidation of sodium sulphite. The reaction was also studied by J. H. Mathews and M. E. Weeks. M. Trautz, and H. L. J. Bäckström discussed the action of light on chemical reactions; and A. J. Allmand and R. E. W. Maddison concluded that light has no effect on the oxidation of aq. soln. of sodium sulphite, and the cases discussed by J. H. Mathews and fellow workers are attributed to an incomplete control of the reaction in darkness, and not to the accelerating influence of ultra-violet light.

According to K. H. Butler and D. McIntosh, sodium sulphite is insoluble in liquid **chlorine,** and has no influence on its b.p. A. W. Francis found the velocity constant in the oxidation of sodium hydrosulphite by **bromine** to be 8·6. The soln. of sodium sulphite is a powerful reducing agent, and the salt is usually transformed into sulphate. Thus, M. Braune, and W. Spring found that the aq. soln. is oxidized to sulphate by **iodine**; W. B. Giles and A. Schearer represented the reaction $Na_2SO_3+I_2+H_2O=Na_2SO_4+2HI$. R. Huerre found a cold 10 per cent. soln. of sodium sulphite dissolves no **sulphur,** and a boiling soln. dissolves only a trace. E. Divers said that if heated in an atm. with an excess of **sulphur dioxide,** at 190°, the sulphite furnishes free sulphur, and sodium sulphate; and in the presence of less sulphur dioxide, sodium thiosulphate is formed. E. C. Franklin and C. A. Kraus found that the anhydrous salt is insoluble in liquid **ammonia;** N. R. Dhar measured the solubility of ammonia in soln. of potassium sulphite. A. Klemenc observed that the rate of oxidation of sulphite soln. by **nitric oxide** decreases with increasing alkalinity of the soln. E. Divers found that when heated with **phosphorus trichloride,** it forms sodium chloride and phosphate. F. E. Brown and J. E. Snyder found sodium sulphite is not affected by **vanadium oxytrichloride.** F. Feigl discussed the oxidation of the sulphites by **carbon** as blood charcoal. The anhydrous salt is insoluble in **alcohol**; J. L. Casaseca found it to be insoluble in **ethyl acetate**; and A. Naumann, insoluble in **methyl acetate,** and **benzonitrile.** W. Eidmann, and A. Naumann found that it is insoluble in **acetone.** G. Romeo and E. d'Amico examined its action on **aldehydes** and **ketones.**

P. Neogi and R. C. Bhattacharyya observed that **magnesium amalgam** does not reduce the sulphite to sulphide. S. Miyamoto found that the rate of oxidation of mixtures of **stannous chloride** and sodium sulphite in alkaline soln. is less than is the case with either salt alone, except when the conc. of the stannous chloride is low. M. Hönig and E. Zatzek, and A. Longi and L. Bonavia, studied its reducing action on soln. of **potassium permanganate** in alkaline soln. F. Haber and F. Bran examined the autoxidation of soln. of sodium sulphite coupled with sodium arsenite, or nickelous hydroxide. J. Pinnow found that a low acidity favours the oxidation of sodium sulphite by a **ferric salt.** *p*-Benzoquinone, quinol, and their respective sulphonic acids function as carrier-catalysts in the oxidation of a sulphite to sulphate by means of a ferric salt, and their effects increase with increase in their respective amounts present. In acid soln., their catalytic action is less pronounced. The increased yield of sulphate in the presence of *p*-benzoquinone is not in accord with the suggestion of C. E. K. Mees and S. E. Sheppard that a dithionate is formed from benzoquinone and a sulphite. N. N. Mittra and N. R. Dhar studied the sympathetic reactions in which mercuric chloride and sodium sulphite as primary reactions are accelerated in the presence of the secondary reaction of mercuric chloride with sodium arsenite or arsenious acid.

J. L. Gay Lussac and J. J. Welter, and J. S. Muspratt saturated a soln. of sodium carbonate with sulphur dioxide and obtained **sodium hydrosulphite,** $NaHSO_3$. B. W. Gerland obtained the same salt, contaminated with 0·41 per cent. P_2O_5, by treating a soln. of sodium phosphate in a similar manner. H. P. Stevens found commercial sodium hydrosulphite contained some pyrosulphite. T. Sabalitschka and G. Kubisch observed that aq. soln. of the hydrosulphite slowly lose the odour of sulphur dioxide, and deposit crystals of sodium sulphate. R. E. Evans and C. H. Desch, and W. Schüler and A. Wilhelm said that if the soln. be vigorously cooled, efflorescent cubic crystals of the *tri-hydrate* are formed. R. de Forcrand gave for the heat of formation SO_2 (64 grms. per 4 litres) and Na_2O (31 grms. per two litres), 16·62 Cals.; and J. Thomsen, 15·9 Cals. R. de Forcrand always obtained the pyrosulphite by slowly evaporating a soln. of sodium carbonate or hydroxide saturated with sulphur dioxide; and he obtained the same thermal value for the reaction between an eq. of sodium hydroxide and a soln. of the supposed hydrosulphite and a soln. of the pyrosulphite. The pyrosulphite undergoes no change on soln., and therefore sodium hydrosulphite does not exist in soln., but is immediately converted into the pyrosulphite. According to F. Ephraim and C. Aellig, the yellow colour of soln. of sodium hydrosulphite is a characteristic property of the soln. and not due to impurity. The colour is always obtained, using the purest materials, when sodium, potassium, or ammonium hydroxide soln., or the soln. of their carbonates, sulphites, formates, and acetates, are saturated with sulphur dioxide. To a less extent, the colour is obtained with soln. of calcium hydroxide and zinc acetate, but not with those of the chlorides, sulphates, and nitrates of the alkali metals nor with hydroxides of the alkaline-earth metals (except calcium), magnesium, or cadmium. The colour reaches its maximum when 5*N*-soln. of alkali hydroxides are sat. with sulphur dioxide, and is not perceptible with soln. below 0·5*N*. Spectroscopically, the colour is very similar to a dil. chromate soln. On dilution, the soln. does not follow Beer's law, for the colour rapidly disappears. The colour may be due to the formation of complexes which in soln. gives a colour three hundred times as intense as that of sodium hydrosulphite at the same conc. There is insufficient evidence to afford a satisfactory explanation of the colour. A. Hantzsch attributes the colour changes, which occur with many salts, to polymerization. In contradistinction to the sulphate and the selenite, which possess the typical yellowish-green colour of the unimolecular salts, the 5-phenyl-10-methylacridinium sulphite can be obtained only as a dark green or a brown modification. The dark green sulphite, which separates from aqueous or alcoholic solution, is changed to the brown form in chloroform, whilst the converse change of the brown to the green is slowly accomplished by alcohol or ether. The molecular complexity of these forms cannot be determined, and it is assumed that the brown sulphite, like the brown iodide, is termolecular; the dark green sulphite is regarded as bimolecular. G. A. Barbaglia and P. Gucci observed that in a sealed tube at 150°, the sat. aq. soln. furnishes sodium sulphate, sulphur, and sulphuric acid. K. Barth found that the electrical conductivity of aq. soln. is in harmony with the assumption that two ions: $NaHSO_3 = Na^{\cdot} + HSO_3'$, are present. For the conductivity, μ, of a mol of the salt in v litres of water, at 25°, he found:

v . .	32	64	128	256	512	1024
μ . .	101·9	106·5	110·7	114·7	118·6	122·8

A. Miolati and E. Mascetti made measurements and obtained similar results and gave $\mu_\infty = 111{\cdot}7$. The results agree with the dibasicity of the acid. According to J. S. Muspratt, the hydrosulphite gives off sulphur dioxide in air, and when heated it gives off sulphur, and sulphur dioxide, leaving a residue of sodium sulphate. A current of an indifferent gas drives sulphur dioxide from the aq. soln. The salt dissolves in water less readily than sodium hydrocarbonate, and is precipitated from its aq. soln. by alcohol. A. W. Francis studied the rate of the oxidation of the hydrosulphite by bromine. G. Scurati-Manzoni found that the aq. soln. is reduced to hyposulphite by a zinc-copper couple; and P. Neogi and R. C. Bhattacharyya, that magnesium amalgam does not reduce the hydrosulphite to sulphide. G. Romeo and E. d'Amico examined its action on aldehydes and ketones. M. Coulouma found that when properly stored, the hydrosulphite can be preserved without decomposition. E. Isnard observed the changes in a conc. soln. of sodium hydrosulphite which occur when it is kept for some time. T. Ito studied the action of sodium hydrosulphite on silver nitrate, and copper sulphate in media containing various lyophilic colloids, gelatin, and hydrosol of ferric oxide.

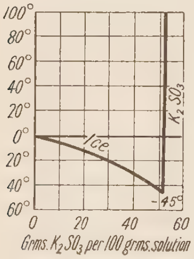


FIG. 67.—Solubility Curves of Potassium Sulphite.

M. Berthelot prepared anhydrous **potassium sulphite,** K_2SO_3, by the method employed for the corresponding sodium salt. The hexagonal crystals are deliquescent, and less oxidizable than when in soln. The heat of formation is (2K,S,3O)=136·30 Cals.; and P. J. Hartog gave −1·75 Cals. for its heat of soln. in 60 parts of water at 18°. J. Danson, and M. Berthelot precipitated an aq. soln. of the salt with ether, and obtained the *monohydrate,* $K_2SO_3.H_2O$. A. F. de Fourcroy and L. N. Vauquelin, J. S. Muspratt, etc., prepared the *dihydrate,* $K_2SO_3.2H_2O$, by passing sulphur dioxide into a dil. soln. of potassium carbonate until all the carbon dioxide had been displaced, and then evaporating the soln. out of contact with air. The salt was previously obtained by G. E. Stahl, T. Bergman, and C. L. Berthollet, and in the early literature it was sometimes called *sal sulphuratum Stahlii,* or *Stahl's sulphur salt.* It was also made, admixed with more or less sulphate, by T. Thomson, and J. J. Bernhardi. The crystals were described by J. S. Muspratt as rhombic octahedra; the salt is deliquescent, and has a penetrating acid, and sulphureous taste. L. N. Vauquelin said that the salt decrepitates when heated, losing first water, then a little sulphur dioxide, then a small quantity of sulphur, and leaving a reddish mixture of potassium sulphide and sulphate. A. Röhrig represented the reaction: $4K_2SO_3 = K_2S + 3K_2SO_4$, and added that in opposition to J. S. Muspratt, etc., no sulphur dioxide is formed. J. S. Muspratt said that the residue contains some potassium hydroxide, and M. Berthelot added that when heated in an atm. of carbon dioxide at a red-heat, sulphate, polysulphide, and carbonate are formed. A. Röhrig said that the salt becomes anhydrous below 120°. F. M. Raoult found the mol. lowering of the f.p. to be 45·1. F. Martin and L. Metz gave 273 Cals. for the heat of formation of K_2SO_3. M. Berthelot gave for the heat of soln., 0·72 Cal., and for the heat of formation (SO_2,2KOH)=15·92 Cals. at 13°. J. B. Austin discussed the heat of hydration. J. Obermiller measured the hygroscopicity of the salt. A. F. de Fourcroy and L. N. Vauquelin showed that the dihydrate dissolves in its own weight of cold water, and in less than that amount of hot water. C. F. Rammelsberg added that the hot sat. soln. does not deposit any salt on cooling, while the cold sat. soln. deposits some salt when heated and redissolves it on cooling. F. Förster and co-workers gave for the solubility of potassium sulphite in grms per 100 grms. of soln.:

	−30°	−15·0°	−3·9°	0·1°	24°	31·2°	55·8°	97·2°
K_2SO_3 .	51·0	51·30	51·35	51·4	51·37	51·90	52·02	53·22

The results are plotted in Fig. 67 with the eutectic point at −45°. There is no sign of the hydrated salt on these curves. J. L. Casaseca said that the salt is very slightly soluble in alcohol, and insoluble in ethyl acetate; E. C. Franklin and C. A. Kraus also found it to be insoluble in liquid ammonia. A. Geuther said that the aq. soln. has an acid taste. W. Spring and A. Lecrenier observed that the sulphite is oxidized by the sulphur halides; P. Schützenberger, that zinc reduces it to hyposulphite. E. Hene obtained the potassium salt by adding potassium sulphate to a soln. of the calcium salt.

J. S. Muspratt prepared **potassium hydrosulphite,** $KHSO_3$, by passing sulphur dioxide into a conc. soln. of potassium carbonate until effervescence ceases; when alcohol is added to the soln. the salt is deposited as a granular mass of crystals, which are washed with a little alcohol, and dried between bibulous paper. J. C. G. de Marignac found that the monoclinic prisms have the axial ratios $a:b:c = 0·9276:1:2·2917$, and $\beta = 94° 46'$. J. S. Muspratt found that the salt has a saline, not unpleasant, taste. A. Geuther observed that the salt suffers very little change at 100°; at 190°, it decomposes with the evolution of water and sulphur dioxide and acquires a yellow colour. The residue contains sulphur, and sodium thiosulphate and sulphate; $6KHSO_3 = K_2S_2O_3 + 2K_2SO_4 + 2SO_2 + 3H_2O$; and the aq. soln. has a neutral reaction. It is supposed that the hydrosulphite first forms the normal sulphite: $2KHSO_3 = K_2SO_3 + SO_2 + H_2O$; and that one equivalent of sulphur dioxide then reacts with three equivalents of the normal sulphite to form the thiosulphate: $3K_2SO_3 + SO_2 = 2K_2SO_4 + K_2S_2O_3$. The reaction between the sulphites and sulphur dioxide has been qualitatively confirmed by E. Divers. If the thiosulphate be more strongly heated, the thiosulphate yields sulphate and sulphide. The formation of a sulphide by the action of heat on thiosulphates has been cited as an argument that the metallic radicle in these compounds is in direct union with sulphur. It has been questioned whether the meta-bisulphites (or pyrosulphites) yield a thiosulphate when heated—A. Geuther said "Yes," M. Berthelot, "No." However, in the formation of a sulphide when a normal sulphite is strongly heated, possibly an alkali oxide is formed, and there is a secondary reaction between sulphur dioxide and the undecomposed sulphite. If the salt be heated over the naked flame, sulphate and polysulphide are formed, and the aq. soln. has an alkaline reaction. J. H. Platt and D. Hudson gave for the solubility S grms. per 100 grms. of water, 45·5 at 15°; 51·5 at 25°; 67·4 at 50°; 76·5 at 60°; 85·6 at 70°; and 91·5 at 75°. K. Barth gave for the mol. conductivity, μ, of a mol of the salt in v litres of water at 25°.

v . .	32	64	128	256	512	1024
μ . .	108·6	113·5	118·0	122·3	126·4	129·8

A. Miolati and E. Mascetti obtained concordant results and gave $\mu_\infty = 135·4$. The results agree with the dibasicity of the acid. A. Miolati and E. Mascetti measured the conductivity of sulphurous acid as it is progressively treated with alkali, and the results, Fig. 57, indicate the existence of hydrosulphite and pyrosulphite. S. S. Bhatnagar and C. L. Dhawan studied the mol. magnetization; and calculated the mol. radius to be 2·58 A. The salt is insoluble in alcohol. C. St. Pierre observed the formation of potassium trithionate in the spontaneous reduction of the hydrosulphite. According to F. M. Raoult, the mol. lowering of the f.p. is 32·5. M. Berthelot found for the heat of formation from 2 mols of K_2SO_3 and 2 mols of HCl, −1·80 Cals.; and from 2 mols of K_2SO_3 and 9 mols of HCl, −2·40 Cals. The heat of neutralization of a mol each of KOH and H_2SO_3 is 16·6 Cals. at 13°. According to M. Berthelot, thermochemical data show that the hydrosulphite, described by J. C. G. de Marignac, and C. F. Rammelsberg, is really the pyrosulphite, and he maintained that the solid hydrosulphite has not been prepared. The hydrosulphite prepared from equimolar parts of sulphur dioxide and potassium hydroxide in aq. soln. is slowly transformed into a soln. which behaves just like a soln. of the solid pyrosulphite; and the change is attended by the evolution of 5·2 Cals. of heat. A. Geuther said that the aq. soln. has an acidic reaction not neutral as stated by J. S. Muspratt. D. Gernez showed that when an indifferent gas is passed through the aq. soln. it loses sulphur dioxide. R. J. Phillips studied the stability of aq. soln. of the salt.

G. T. Morgan and J. D. M. Smith passed sulphur dioxide into a soln. of rubidium carbonate until a pale green soln. was acquired; alcohol was added, and a voluminous, white precipitate consisting of colourless prisms of **rubidium hydrosulphite,** $RbHSO_3$, was formed. The salt is freely soluble in water; and the aq. soln. reacts acid to litmus and phenolphthalein, and neutral to methyl orange. When the dry salt is gradually heated to redness, it gives off water, sulphur, and sulphur dioxide, leaving a residue of rubidium sulphate. If rubidium hydrosulphite be added to an eq. proportion of a soln. of the carbonate; heated to expel carbon dioxide, and treated, when cold, with an excess of absolute alcohol, a heavy, oily liquid is precipitated, and this freezes to a colourless, crystalline mass, which when washed with a mixture of alcohol and ether, and dried over calcium chloride, furnishes **rubidium sulphite hemialcoholate,** $2Rb_2SO_3.C_2H_5OH$. The alcoholate gives off its alcohol when heated, and is freely soluble in water. If a sat. aq. soln. of the alcoholate be evaporated by boiling under reduced press., small, colourless, prismatic tablets of anhydrous **rubidium sulphite,** Rb_2SO_3, are precipitated. The salt is freely soluble in water and aq. alcohol, it reacts alkaline to litmus, gives off sulphur dioxide when treated with dil. mineral acids, and on ignition gives a residue of rubidium sulphate and sulphide.

C. Chabrié dissolved 14 grms. of cæsium carbonate in 400 c.c. of 99 per cent. alcohol, divided the soln. into 2 halves, and saturated one-half at the b.p. with sulphur dioxide, and mixed the two halves, distilled off the alcohol, and dried the residue in vacuo. The white, crystalline mass of **cæsium sulphite,** Cs_2SO_3, dissolves in its own weight of water at 100°. If the above operations be conducted in aq. soln. the crystalline product, mixed with some sulphate, contains 9·29 per cent. of water. The half of the alcoholic soln., just indicated, when sat. with sulphur dioxide gives white crystals of **cæsium hydrosulphite,** $CsHSO_3$, which are freely soluble in water, and less soluble in alcohol.

P. J. Hartog prepared **ammonium sodium hydrosulphite,** $(NH_4)Na_2H(SO_3)_2.4H_2O$, from mixed soln. of sodium and ammonium sulphites; and H. Schwicker, by passing ammonia into a conc. soln. of sodium hydrosulphite, or by partially saturating a conc. soln. of ammonium hydrosulphite with sodium carbonate. G. Tauber, on an industrial scale, passed ammonia and sulphur dioxide into a cooled soln. of sodium chloride. The analyses by J. C. G. de Marignac agree with the above formula, but the salt prepared by G. Tauber was represented by the formula $2Na_2SO_3.(NH_4)_2S_2O_5.10H_2O$. Indeed most of the complex salts here described can be regarded as pyrosulphites of analogous composition. According to P. J. Hartog, there are two isomeric forms with a difference of 2·74 Cals. in their heats of formation. This salt crystallizes in large plates which, according to J. C. G. de Marignac, belong to the monoclinic system, and have the axial ratios $a:b:c=1·8682:1:2·8501$, and $\beta=152°\ 12'$. A. Schwicker said that the salt is moderately stable at ordinary temp., but at 130° it is quickly decomposed with the evolution of water, ammonia, and sulphur dioxide. Water dissolves 42·3 per cent. at 12°, and 48·5 per cent. at 15°. P. J. Hartog gave $-30·72$ Cals. for the heat of soln. of one part of the salt in 40 parts of water at 20°. The aq. soln. has an acid reaction. P. J. Hartog said that only in the presence of a large excess of ammonia is it possible to obtain crystals of **ammonium potassium sulphite,** $(NH_4)K(SO_3)_2.nH_2O$, from a soln. of the component salts. The observed composition is not constant, indicating that solid soln. of the component salts are involved. Hence the existence of this salt as a chemical individual is in doubt. The hexagonal prisms actually obtained when heated in a sealed tube give a sublimate of ammonium sulphite.

W. Spring obtained an impure sodium potassium sulphite by reducing potassium thiosulphate or trithionate with sodium amalgam—some mixed sulphide was formed at the same time. P. J. Hartog prepared anhydrous **sodium potassium sulphite,** $KNaSO_3$, from a soln. containing the correct proportions of sodium hydrosulphite and potassium hydroxide. K. Barth obtained it in a similar way, using either sodium hydrosulphite and potassium hydroxide or potassium hydrosulphite and sodium hydroxide. P. J. Hartog gave for the heat of formation in aq. soln., $Na_2SO_3+K_2SO_3=2NaKSO_3+3·76$ Cals.; and $-1·19$ Cals. for the heat of soln. at 18°. H. Schwicker obtained yellow crystals of the *monohydrate,* $NaKSO_3.H_2O$, by exactly neutralizing a soln. of sodium hydrosulphite with potassium carbonate, and evaporating over sulphuric acid; and K. Barth, by cooling a soln. of potassium hydrosulphite with the theoretical proportion of sodium hydroxide. A. Schwicker prepared yellowish crystals of the *dihydrate* by evaporating over sulphuric acid a conc. soln. of potassium hydrosulphite mixed with the stoichiometrical proportion of sodium carbonate. A. Röhrig obtained the salt from a mixed soln. of the carbonate of the one metal with the hydrosulphite of the other, by precipitation with alcohol or ether. K. Barth said that the anhydrous salt is obtained by the alcohol precipitation process. He obtained the dihydrate by evaporating over sulphuric acid a soln. of the theoretical proportions of sodium hydrosulphite and potassium hydroxide. A. Schwicker said that the salt obtained from potassium hydrosulphite and sodium carbonate gives, when heated with ethyl iodide at 140°, a compound $KO.C_2H_5SO_2.\frac{1}{4}NaI$, which crystallizes from hot alcohol in colourless needles. On the other hand, the salt obtained from sodium hydrosulphite and potassium hydroxide yields under similar circumstances $NaO.C_2H_5SO_2.\frac{1}{4}KI$. It was assumed that in the former case the sodium was directly connected with the sexivalent sulphur, and in the latter case, the potassium was directly bound to the sexivalent sulphur. G. S. Fraps, A. E. Arbusoff, and M. H. Godby could not confirm these conclusions, for, in repeating the work, they obtained no evidence of the existence of two isomeric sulphites. In any case, K. Barth found that the aq. soln. of the two salts are identical, and, in particular, that they have the same electrical conductivity:

v . .	0·25	2·5	1·0	2·0	8	32	64	256	512	1024
μ . .	37·6	51·0	61·8	70·1	85·3	99·1	104·1	113·6	116·3	117·7

as they should do on the ionization hypothesis, since in dil. soln. they yield the ions $K^{\cdot}$, $Na^{\cdot}$, and SO_3''. P. J. Hartog prepared transparent prisms of **sodium potassium hydrosulphite,** $K_2NaH(SO_3)_2.3H_2O$, by crystallization from a conc. soln. of $NaKSO_3$, and an eq. of $KHSO_3$. P. J. Hartog obtained $Na_2KH(SO_3)_2.4H_2O$ from a soln. of 2 eq. sodium carbonate sat. with sulphur dioxide, mixed with one eq. of potassium carbonate. A. Schwicker obtained it in transparent prisms when a conc. soln. of eq. quantities of sodium potassium sulphite and potassium hydrosulphite is evaporated over sulphuric acid; it behaves like the double salts described above. According to P. J. Hartog, this salt cannot be dehydrated without decomposition; it loses no water of crystallization in dry nitrogen at 90°, and at 100°–110° there is a loss of 26·65 per cent. along with some sulphur dioxide. The heat of formation is $K_2O_{soln.}+2(Na_2O.2SO_2)_{soln.}=K_2O.2Na_2O.4SO_{3soln.}+61·81$ Cals.; and $2Na_2SO_{3cryst.}+K_2S_2O_{5cryst.}+9H_2O_{liquid}=K_2O.2Na_2O.3SO_3.9H_2O+25·88$ Cals.

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§ 17. The Sulphites of the Copper Family

A. F. de Fourcroy and L. N. Vauquelin[1] observed that a yellowish-red precipitate is formed when a soln. of cupric sulphate is treated with an alkali sulphite and, for a time, it was considered to be a copper sulphite. The product was investigated by M. E. Chevreul, J. S. Muspratt, O. Döpping, C. F. Rammelsberg, etc. It is probably a mixed salt—*vide infra*. The normal **copper sulphite,** $CuSO_3$, has not been obtained in a stable form in aq. media. G. T. Morgan and F. H. Burstall showed that the cupric ion is reduced, forming a red precipitate of cuprosic sulphite, $Cu(CuSO_3)_2.2H_2O$. The stability is enhanced by ammination, for P. Pudschies prepared **cupric tetramminosulphite,** $[Cu(NH_3)_4]SO_3.2H_2O$, by the action of sodium sulphite on a soln. of cupric tetramminoacetate. The salt is hydrolyzed by water. The partition coeff. with chloroform was measured ; and the electrical conductivity at 18° of a mol of the salt in v litres of ammoniacal soln. was found to be :

v . .	5·276	10·552	21·104	42·208	84·416	168·832
μ . .	47·4	57·3	65·6	74·7	85·2	ppt.

G. T. Morgan and F. H. Burstall also prepared **copper aquoethylenediaminosulphite,** $[Cu(H_2O)en]SO_3$, by the action of an aq. soln. of ethylenediamine on cuprosic sulphite; and **copper bisethylenediaminosulphite,** $[Cuen_2]SO_3$, by adding copper to a suspension of silver sulphite in ethylenediamine. This is the more stable of the two salts. The aq. soln. of the aquoethylenediaminosulphite decomposed on warming to give a brown precipitate containing cuprous oxide; dil. sulphuric acid caused a separation of red metallic copper, whereas hydrochloric acid gave cuprous chloride, both reactions being accompanied by evolution of sulphur dioxide. On exposure to air this sulphite oxidized slowly; at 100° it blackened, and at higher temp. its colour changed to brown. Copper bisethylenediaminosulphite is hygroscopic, but it remained unchanged in a closed vessel; its aq. soln. was not visibly affected by boiling. In cold soln. of the salt, silver nitrate, and barium chloride produced, respectively, copious white precipitates of silver and barium sulphites. With sodium hydroxide the soln. remained clear, but its colour changed from purple to blue; the colour was discharged by mineral acids. A. Étard showed that when sulphur dioxide is passed into a soln. of cupric acetate, a complex cuprosic sulphite is formed. By varying the temp. and relative proportions of acid and water, a whole series of basic salts can be obtained with colours varying from light-brown to deep violet. If the soln. is very dilute, cuprous oxide is formed. All these basic salts are perfectly homogeneous and crystallize well, but the proportion of copper varies as if their composition was governed by the physical conditions and not by the laws of chemical combination. One of these salts was obtained several times in violet crystals of **cuprous enneoxysulphite,** $Cu_2O.Cu_2SO_3$. When sulphur dioxide is passed into a boiling, sat. soln. of basic cupric acetate in acetic acid of sp. gr. 1·06, the soln. becomes blue, and a heavy precipitate of white, nacreous plates is formed. The passage of the gas is discontinued before this precipitate is converted into the violet basic salt; the liquid is decanted off, and the precipitate is washed successively with water, alcohol, and ether. The product is **cuprous sulphite,** $Cu_2SO_3.H_2O$. It forms colourless or pale amber hexagonal plates which act on polarized light, and have a sp. gr. 3·83 at 15°. J. B. Ragojsky obtained a red cuprous sulphite by treating ammonium cuprous sulphite with sulphurous acid, but L. P. de St. Gilles, C. F. Rammelsberg, and N. Svensson could not verify this. A. Étard observed that by prolonged and repeated digestion with sulphurous acid, the ammonium cuprosic sulphite first formed is completely converted into brick-red, prismatic crystals of $Cu_2SO_3.H_2O$, which act on polarized light, and have a sp. gr. 4·46 at 15°. The red sulphite is more readily obtained by the action of sulphurous acid on sodium cuprous sulphite. Cuprous sulphite exists, therefore, in two isomeric modifications which differ in colour and sp. gr. The white modification may be converted into the red by prolonged digestion with sulphurous acid in sealed tubes. The white salt corresponds with the white cuprous chloride and acetate, and is the normal cuprous sulphite. The red salt, *cuprous isosulphite,* is in all probability a polymeride, $(Cu_2SO_3)_8.8H_2O$, because, when treated with a conc. soln. of sodium sulphite, it forms a brown octosulphite, $Cu_6Na_{16}H_{10}S_8O_{28}.43H_2O$; whereas the white, normal sulphite furnishes white $Na_2Cu(SO_3)_2.H_2O$. J. B. Rogojsky said that the red sulphite forms a colourless soln.; and when the hydrochloric acid soln. is diluted, it forms a colourless liquid; G. Kroupa found that the salt is soluble in sulphurous acid; and G. Denigès, that it forms unstable, complex salts with pyridine. S. B. Newbury thought that the brown precipitate formed by the action of boiling water on $3CuO.2SO_3.1\frac{1}{2}H_2O$, is cuprous sulphite; hydrochloric acid converts it into cuprous chloride.

It is possible that many of the complex copper sulphites are solid soln., not chemical individuals. J. B. Ragojsky prepared anhydrous **ammonium cuprous sulphite,** $(NH_4)_2SO_3.Cu_2SO_3$, or $(NH_4)CuSO_3$, by adding cupric sulphate to an excess of ammonium sulphite and adding more cupric sulphate and warming the soln. so as to dissolve the yellow precipitate. Six-sided, colourless plates separate from the soln., and they can be washed with cold water. He also made it by precipitating cupric sulphate with an excess of ammonium sulphite and passing sulphur dioxide through the brown mixture until it is colourless; and by passing sulphur dioxide, for not too long, through an ammoniacal soln. of cuprosic sulphite; L. P. de St. Gilles, and H. Vohl also prepared this salt. D. Vorländer and F. Meyer obtained this salt by saturating with sulphur dioxide a soln. of 70 grms. copper sulphate in 300 c.c. of water, and 140 c.c. of 33 per cent. aq. ammonia; adding 100–130 c.c. more aq. ammonia, and passing sulphur dioxide until the liquid became colourless, and cooling the soln. A. Rosenheim and S. Steinhäuser mixed a mol of freshly precipitated cupric carbonate with a soln. of 6–8 mols of ammonium hydrosulphite. The white crystals are stable in air; they form a basic cuprosic salt with boiling water; conc. sulphuric acid forms copper and cupric sulphate; copper sulphate soln., cuprosic sulphate; sulphur dioxide forms cuprous sulphite; acids dissolve the salt with the evolution of sulphur dioxide. A. Commaille prepared the *hydrate*, $(NH_4)Cu(SO_3).H_2O$, by passing sulphur dioxide into an ammoniacal soln. of cupric sulphate, or into an ammoniacal soln. of cupric acetate decolorized by copper; and A. Étard, by boiling a soln. of cuprosic sulphite with conc. ammonium hydrosulphite, and washing the six-sided, colourless plates successively with water, alcohol, and ether. The crystals are stable in air.

F. L. Hahn and co-workers prepared complexes with ammonium and copper sulphites by adding an excess of the alkali sulphite to a soln. of the metal sulphite in ammonia, alkali acetate, or acetic acid, and evaporating off the ammonia or sulphur dioxide when necessary. H. Böttinger prepared **diammonium tetracuprous trisulphite,** $(NH_4)_2SO_3.2Cu_2SO_3.2H_2O$, from a mixture of a soln. of cupric sulphate and an excess of ammonium sulphite with enough sulphurous acid to prevent precipitation on warming, or allowing the soln. to stand in a closed vessel, the salt appears in white plates, which, when heated, form cuprosic sulphite. J. S. Muspratt prepared the same salt; but N. Svensson thinks that the salt is impure ammonium cuprous disulphite. A. Rosenheim and S. Steinhäuser obtained **tetrammonium dicuprous trisulphite,** $2(NH_4)_2SO_3.Cu_2SO_3.3H_2O$, in yellow needles, from a mol of freshly precipitated cupric carbonate and 15 mols of ammonium hydrosulphite. N. Svensson obtained **pentammonium cuprous trisulphite,** $(NH_4)_5Cu(SO_3)_3.H_2O$, in yellow needles, from a soln. of cuprosic sulphate and ammonium sulphite mixed with aq. ammonia; A. Rosenheim and S. Steinhäuser, **dodecammonium dicuprous heptasulphite,** $6(NH_4)_2SO_3.Cu_2SO_3.4H_2O$, in pale yellow needles, from the mother-liquor obtained in preparing *dihydrated* **heptammonium cuprous tetrasulphite,** $(NH_4)_7Cu(SO_3)_4.2H_2O$, in white needles, and cooling the soln., by boiling cuprosic sulphite with normal ammonium sulphite; the *pentahydrate*, $(NH_4)_7Cu(SO_3)_4.5H_2O$, in white needles, was obtained by L. P. de St. Gilles from a mixed soln. of cuprous chloride and an excess of ammonium sulphite; N. Svensson, by passing sulphur dioxide into a soln. of cupric tetramminoxide. A. Rosenheim and S. Steinhäuser could not confirm this; but it was obtained by N. Svensson, by adding cupric sulphate or cuprosic sulphite to an excess of a soln. of ammonium sulphite. A. Étard prepared **lithium cuprous sulphite,** $LiCuSO_3.H_2O$, by boiling a soln. of cuprosic sulphite with a conc. soln. of lithium hydrosulphite, and washing the precipitate successively with water, alcohol, and ether. F. L. Hahn and co-workers prepared complexes with sodium sulphite as in the case of the ammonium complexes. A. Commaille made **sodium cuprous sulphite,** $NaCuSO_3.H_2O$, by adding a conc. soln. of cupric acetate to a conc. soln. of sodium sulphite so long as the precipitate dissolves. The green soln. is gradually decolorized, and furnishes colourless crystals. N. Svensson, and A. Rosenheim and S. Steinhäuser obtained it by the action of a conc. soln. of sodium hydrosulphite on cupric carbonate; and A. Étard, by boiling cuprosic sulphite with a conc. soln. of sodium hydrosulphite. The salt is fairly stable but decomposed by water. A. Commaille obtained the *hemihenahydrate* in colourless or white quadratic plates, by leaving the preceding salt in contact with its mother-liquor: N. Svensson, from a boiling soln. of cuprosic sulphite in a conc. soln. of sodium sulphite—A. Rosenheim and S. Steinhäuser obtained a similar salt but of variable composition; and A. Étard, by the action of a conc. soln. of sodium hydrosulphite on cuprous sulphite. A. Rosenheim and S. Steinhäuser obtained yellow, microscopic crystals of **tetrasodium decacuprous heptasulphite,** $2Na_2SO_3.5Cu_2SO_3.30H_2O$, by the action of a sat. soln. of 2 mols of sodium hydrosulphite on a mol of freshly-precipitated cupric carbonate; and **hexasodium tetracuprous pentasulphite,** $3Na_2SO_3.2Cu_2SO_3.29H_2O$, by the action of sulphur dioxide on conc. soln. of cupric sulphate and sodium carbonate cooled by ice; and N. Svensson, by the action of sulphur dioxide on a soln. of cuprosic sulphite in a conc. soln. of sodium sulphite. J. S. Muspratt obtained yellow crystals of **pentasodium cuprous trisulphite,** $Na_5Cu(SO_3)_3.19H_2O$, by treating with a conc. soln. of sodium sulphite the soln. obtained by passing sulphur dioxide into water with cupric hydroxide in suspension, mixing the liquid with absolute alcohol, and allowing the soln. to stand in vacuo. N. Svensson said that the product is really cuprosic sulphite, but he obtained the salt by adding a soln. of sodium sulphite to one of cupric sulphate so long as the yellow precipitate dissolves, adding alcohol, and evaporating over sulphuric acid and calcium chloride. N. Svensson also reported **heptasodium cuprous tetrasulphite,** $Na_7Cu(SO_3)_4.9\frac{1}{2}H_2O$, in needle-like crystals, by adding alcohol to the mother-liquor from hemihenahydrated sodium cuprous sulphite; and A. Étard obtained **sodium cuprous hydroctosulphite,** $Na_{16}Cu_6H_{10}S_8O_{24}.43H_2O$, by treating the red cupric sulphite with a conc. soln. of sodium hydrosulphite, and washing successively with water, alcohol, and ether.

M. E. Chevreul obtained a yellow precipitate with a not too dil. mixture of cupric nitrate and potassium sulphite. F. J. Otto represented the precipitate obtained with copper sulphate and potassium hydrosulphate as **potassium cupric trisulphite,** $2K_2SO_3.CuSO_3$. N. Svensson said that this product is a mixture. F. L. Hahn and co-workers obtained complexes with potassium sulphite as in the case of the complexes with the ammonium sulphite. A. Étard obtained **potassium cuprous sulphite,** $KCuSO_3.H_2O$, by boiling cuprosic sulphite with a conc. soln. of potassium hydrosulphite and washing successively with water, alcohol, and ether. A. Rosenheim and S. Steinhäuser saturated with sulphur dioxide a mixture of a conc. soln. of cupric sulphate and an excess of potassium carbonate cooled by a freezing mixture; and they obtained the same salt by the action of a mol of cupric sulphate and 10 or more mols of potassium hydrosulphite. N. Svensson reported **tripotassium cuprous dihydrotrisulphite,** $K_3H_2Cu(SO_3)_3.2\frac{1}{2}H_2O$, to be formed in yellow needles by treating freshly precipitated cupric carbonate with a soln. of potassium hydrosulphite saturated with sulphur dioxide; if an excess of the potassium hydrosulphite is used, or if a soln. of potassium carbonate be mixed with cupric carbonate and sat. with sulphur dioxide, while cooled with ice, **tetrapotassium cuprous trihydrotetrasulphite,** $K_4CuH_3(SO_3)_4$, is formed as a crystalline mass decomposed by water. C. F. Rammelsberg reported crystals of $8K_2SO_3.Cu_2SO_3.16H_2O$, to be formed by digesting the yellow precipitate, obtained by the action of potassium sulphite on a soln. of cupric salt, with a conc. soln. of potassium sulphite, but A. Rosenheim and S. Steinhäuser showed that the product is a mixture.

According to H. Baubigny, when aq. soln. of 4 grms. of copper sulphate and 13 grms. of sodium sulphite are mixed in a sealed tube at ordinary temp., in a few hours, colourless crystals of **sodium cuprous sulphite,** $Na_2SO_3.CuSO_3.12H_2O$, or $NaCuSO_3.6H_2O$, are formed, and the liquid contains the amount of dithionate indicated by: $2CuSO_4+4Na_2SO_3=2Na_2SO_4+Cu_2SO_3.Na_2SO_3+Na_2S_2O_6$. The double sulphite is unstable, and, on exposure to air, it is oxidized with the loss of water. If the initial substances are mixed in hot soln. a colourless liquid results and a red precipitate is formed as a decomposition product of the sodium cuprous sulphite first formed. Its composition is $Cu_2(OH)_2.Cu_2SO_3.5CuSO_3.4H_2O$.

It was formerly assumed that the products obtained by A. F. de Fourcroy and L. N. Vauquelin, M. E. Chevreul, P. Berthier, and J. S. Muspratt, by the action of warm sulphurous acid on cupric oxide, hydroxide, or carbonate, were more or less impure cuprous sulphite. M. E. Chevreul gave $4Cu_2O.5SO_2.5H_2O$; and J. S. Muspratt, $Cu_2SO_3.H_2O$; H. Böttinger, and O. Döpping, $3Cu_2O.4SO_2.4H_2O$; N. A. E. Millon and A. Commaille said that the product contained up to about 6 per cent. of cupric sulphate which could not be removed by washing. C. F. Rammelsberg treated the soln. with ether and obtained what he regarded as *dihydrated* **cuprosic sulphite,** $Cu_2SO_3.CuSO_3.2H_2O$, and this was confirmed by L. P. de St. Gilles, J. B. Rogojsky, and N. Svensson. According to S. B. Newbury, if moist cupric hydroxide, free from sulphate, is treated with sulphurous acid cooled by a freezing mixture, it becomes yellow, and then forms a dark green liquid which, after standing several hours at ordinary temp., precipitates the red salt when warmed, while the soln. becomes colourless. Related products were obtained by the action of sulphurous acid on cupric oxide—P. Berthier; cupric hydroxide—R. Böttger, J. S. Muspratt, and A. Vogel. By passing sulphur dioxide into a conc. soln. of cupric sulphate at 100°, F. Binnecker, L. Meyer, F. Wöhler, O. Döpping, T. Parkman, and L. P. de St. Gilles obtained the cuprosic salt. S. B. Newbury passed the gas slowly into a 10 per cent. soln. of cupric sulphate containing a thin strip of copper; E. Paterno and U. Alvisi precipitated the salt by passing the gas into a soln. of cupric fluoride in dil. hydrochloric acid; L. P. de St. Gilles, O. Döpping, T. Parkman, A. Vogel, amd A. Étard by passing the gas rapidly into a soln. of 77 grms. of cupric acetate in a litre of water at 65° until the yellow precipitate first formed has dissolved and allowing the soln. to stand—a red salt is deposited; M. E. Chevreul, by mixing a boiling soln. of potassium or sodium sulphite with copper sulphate or nitrate—J. S. Muspratt used a soln. of ammonium sulphite, and modifications were employed by J. Bourson, H. Böttinger, J. B. Rogojsky, O. Döpping, and K. Seubert and M. Elten; J. B. Rogojsky, and L. P. de St. Gilles, by treating a soln. of ammonium cuprous sulphite with copper sulphate; G. Kroupa, by boiling a soln. of cuprous sulphite with an excess of sulphurous acid; H. Böttinger, J. S. Muspratt, and L. P. de St. Gilles, by boiling a soln. of ammonium cuprosic sulphite with water; L. P. de St. Gilles, by boiling, or allowing to stand, a soln. of cuprous sulphite in sulphurous acid; and K. Seubert and M. Eten, by boiling the filtrate from the basic sulphite. The salt furnishes dark red, garnet-red, cochineal-red, or reddish-brown plates or needles or octahedra —not cubic octahedra. A. Étard gave 3·57 for the sp. gr. at 15°. M. E. Chevreul said that the dry salt is stable in air; and C. F. Rammelsberg found that when heated out of contact with air to 150°, some hygroscopic moisture is expelled; at a higher temp., water and sulphur dioxide are given off; and at a red-heat there remains brown cuprous oxide and cupric sulphate. If heated in hydrogen, copper and its sulphide and sulphate remain. A. Étard said that at 180°, in a current of sulphur dioxide, carbon dioxide or monoxide, cupric oxide and cuprous sulphide are formed; and in hydrogen sulphide, Cu_3S_2 is formed. P. Berthier said that the moist salt in air forms a mixture of neutral and basic cupric sulphate. G. Gin, and M. E. Chevreul found that the salt is sparingly soluble in cold water; and when boiled with water, M. E. Chevreul said that sulphur dioxide, cupric sulphate and sulphide, and cuprous oxide are formed. J. S. Muspratt, H. Böttinger, and O. Döpping made observations on this subject. C. Geitner found that when heated with water in a sealed tube at 200°, crystal plates of copper, and a soln. of cupric sulphite and sulphate are formed. A. Étard, and G. Gin made observations on this subject. G. Gin, and P. Berthier said that the salt is soluble in sulphurous acid; hydrochloric acid, aq. ammonia, and a soln. of cupric sulphate. The ammoniacal soln. is blue; and, according to C. F. Rammelsberg, the hydrochloric acid soln. is brown, and when diluted, green—J. S. Muspratt said that the hydrochloric acid soln. is colourless; and O. Döpping, yellow. The soln. in dil. nitric acid is not attended by the evolution of gas, and it is colourless. L. P. de St. Gilles, and T. Parkman obtained the *pentahydrate*, $CuSO_3.Cu_2SO_3.5H_2O$, from the emerald-green soln. obtained by passing sulphur dioxide into a soln. of cupric acetate.

N. A. E. Millon and A. Commaille did not obtain constant proportions for $Cu^{\cdot}$: $Cu^{\cdot\cdot}$. A. Étard maintained that the red-coloured salt just described is a cuprosic octosulphite, $Cu_{12}S_8O_{24}.26H_2O$.

A. Étard obtained a basic salt *cuprosic oxyoctosulphite*, $Cu_2O.Cu^{\cdot\cdot}{}_{14}Cu^{\cdot}{}_4S_8O_{31}.5H_2O$, as a yellow crystalline precipitate, by passing sulphur dioxide into a soln. of cupric acetate at 85°. M. Berthelot obtained a basic sulphate by the reducing action of copper on sulphuric acid. V. V. Sarma obtained a red, granular precipitate of *cuprosic oxysulphite*, $Cu_2O.CuSO_3.5H_2O$, by the action of sulphur dioxide on yellow cuprous sulphide suspended in dil. alkali-lye.

L. P. de St. Gilles obtained *pentahydrated* **ammonium cuprosic sulphite,** $(NH_4)_2SO_3.2Cu_2SO_3.CuSO_3.5H_2O$, in pale green, rhombic, doubly refracting plates by mixing soln. of cupric sulphate and ammonium sulphite, each saturated with sulphur dioxide; and N. Svensson, by passing the same gas into a soln. of cupric sulphate mixed with not quite enough ammonia to dissolve the precipitate. A. Rosenheim and S. Steinhäuser obtained the *hemitridecahydrate* by passing sulphur dioxide through a conc. soln. of cupric sulphate mixed with ammonia until precipitation begins. A. Étard reported **sodium cuprosic tetrasulphite,** $Na_8Cu_{12}S_4O_{12}.18H_2O$, to be formed in chrome-yellow prisms, by moistening cuprosic sulphate with a conc. soln. of sodium hydrosulphite—not in excess; by shaking a conc., aq. soln. of sodium hydrosulphite with powdered, anhydrous cupric sulphate; and by treating cupric acetate with an excess of a cold, conc. soln. of sodium hydrosulphite; A. Rosenheim and S. Steinhäuser made *hexahydrated* **sodium cuprosic pentasulphite,** $2Na_2SO_3.Cu_2SO_3.2CuSO_3.6H_2O$, in deep yellow crystals, by the action of a sat. soln. of 10 20 mols of sodium hydrosulphite on a mol of freshly precipitated cupric carbonate, and cooling the yellow soln. with ice. They also obtained an *octohydrate* of the same salt. A. Étard obtained dark reddish-brown crystals of **sodium cuprosic octosulphite,** $Na_8Cu_4S_8O_{24}.9H_2O$, by treating red cuprous sulphite with a conc. soln. of sodium hydrosulphite.

J. B. Ragojsky reported **potassium cuprosic heptasulphite,** $K_2SO_3.3Cu_2SO_3.CuSO_3$, to be formed by boiling a soln. of copper sulphate with potassium sulphite; L. P. de St. Gilles obtained **potassium cuprosic tetrasulphite,** $K_2SO_3.2Cu_2SO_3.CuSO_3.5H_2O$, in green prismatic plates, by mixing cupric nitrate with a conc. soln. of potassium sulphite sat. with sulphur dioxide. A. Rosenheim and S. Steinhäuser prepared **potassium cuprosic hexasulphite,** $K_2SO_3.Cu_2SO_3.4CuSO_4.16H_2O$, as a yellow crystalline mass, by mixing conc. soln. of a mol of cupric sulphate and 4·6 to 8 mols of potassium hydrosulphite.

P. Berthier obtained a soln. of **cupric sulphite,** $CuSO_3$, by the action of sulphurous acid on cupric carbonate; and S. B. Newbury said that the soln. is fairly stable at 0°, but the solid salt could not be isolated. N. A. E. Millon and A. Commaille obtained $CuSO_3.2\frac{1}{3}H_2O$, by passing sulphur dioxide into a suspension of cupric hydroxide in alcohol. The green salt is insoluble in water, and is not decomposed by that liquid. P. Pudschies reported a dark blue mass of crystals of **cupric amminosulphite,** $CuSO_3.4NH_3.2H_2O$, from a soln. of cupric tetramminoacetate and sodium sulphite. He measured the electrical conductivity of the soln., and also the partition of ammonia between an ammoniacal soln. of the salt and chloroform. The salt is hydrolyzed by water. A. Étard obtained **cupric oxysulphite,** $CuO.CuSO_3$, by heating the cuprosic sulphite to 180° in an atm. of sulphur dioxide or carbon dioxide or monoxide. K. Seubert and M. Elten obtained **cupric hexahydroxytetrasulphite,** $4CuSO_3.3Cu(OH)_2.5H_2O$, by cooling to 3° a soln. of 24·87 grms. of cupric sulphate and 12·58 grms. of sodium sulphite in a litre of water. The green precipitate readily oxidizes; and dissolves without residue in sulphuric acid. S. B. Newbury prepared **cupric oxydisulphite,** $CuO.2CuSO_3.nH_2O$, from the dark green soln. of cupric sulphite, formed by passing sulphur dioxide through well-cooled water containing precipitated cupric hydroxide in suspension, by exposure to air, or by passing a current of air through the soln., or by adding alcohol to the soln. The salt precipitated has a bright yellow ochre colour, and dries in air to a yellow powder. It dissolves in dil. hydrochloric acid to a green soln., giving off sulphur dioxide without separation of cuprous chloride, and in dil. sulphuric acid without separation of metallic copper. On boiling with water for a few minutes, the compound undergoes complete decomposition, a deep-blue soln. of copper sulphate and a brown, insoluble substance being formed, which, by hydrochloric acid, is completely converted into cuprous chloride with liberation of sulphur dioxide, and dissolves in sulphuric acid with liberation of metallic copper. This substance is in all probability cuprous sulphite, for, on continued boiling with water, sulphur dioxide escapes and bright-red cuprous oxide is formed. When moist basic cupric sulphite is exposed to the air, it is gradually oxidized, forming cupric sulphate, which may be dissolved out by water, leaving a yellowish-green, insoluble powder, which gives all the reactions of the original substance. P. Pudschies treated the dark blue soln. of cupric tetramminosulphite with a sat. soln. of sodium sulphite, and after the liquid had stood some time, he obtained a black product which had a variable composition—possibly *sodium cupric amminosulphite*.

According to A. F. de Fourcroy and L. N. Vauquelin, S. Kern, and P. Berthier, **silver sulphite,** Ag_2SO_3, is formed when a soln. of silver nitrate is treated with an excess of sulphurous acid or an alkali sulphite, and the precipitation is almost quantitative. J. S. Muspratt said that an excess of sulphurous acid tends to decompose the sulphite, and, according to H. Rose, if allowed to stand a long time or boiled with the sulphurous acid, metallic silver is formed; an excess of alkali sulphite dissolves the precipitate. W. H. Sodeau made the sulphite by passing sulphur dioxide into a soln. of silver nitrate; washing the precipitate with warm, distilled water; and drying in vacuo over sulphuric acid. The white precipitate of silver sulphite consists of minute crystals. J. S. Muspratt said the precipitate resembles silver chloride, and is blackened on exposure to light, while A. F. de Fourcroy and L. N. Vauquelin said that sunlight does not affect silver sulphite. W. H. Sodeau observed the blackening of both dry and moist silver sulphite on exposure to sunlight. E. Divers and T. Shimidzu said that silver and mercury sulphites are not like most other inorganic sulphites, in that they are not liable to atm. oxidation. P. Berthier said that the sulphite is decomposed at 100°, whether dry or immersed in water, forming sulphur dioxide, silver, and silver sulphate; S. Kern made a similar observation. W. H. Sodeau observed that the dry or wet sulphite is slightly darkened in an hour at 100°; and blackened in an hour at 130°, in half an hour at 200°, and in a few seconds at 400°. J. S. Muspratt observed that sulphur dioxide is evolved below redness and silver and its sulphate are formed; and at a higher temp., silver, oxygen, and sulphur trioxide are produced. G. N. Lewis and co-workers found that when silver sulphite is decomposed by heat, the reaction does not occur in accordance with the equation: $Ag_2SO_3=Ag_2O+SO_2$, but that the solid product of the reaction is either a basic salt or a solid soln. In presence of water, reaction takes place more rapidly in accordance with the equation $2Ag_2SO_3=2Ag+Ag_2SO_4+SO_2$, this reaction being catalyzed by the water. Sulphuric acid is then produced in consequence of the further reaction represented by $Ag_2SO_4+SO_2+2H_2O=2Ag+2H_2SO_4$. C. Geitner observed that water decomposes it into silver and silver sulphate, and P. Berthier showed that the reaction is faster if some potassium sulphite be present, or, according to J. S. Muspratt, sulphurous acid. In agreement with J. S. Stas, H. Baubigny said that in darkness silver sulphite is stable in the presence of water, but in diffused light it is decomposed, but the decomposition is slower than with heat. J. Bodner said that water alone decomposes the salt only when boiled, and silver is separated. H. Baubigny observed very little sulphur dioxide is formed by the action of boiling water; the main products are silver, silver dithionate, and sulphate. If heated in a sealed tube, the sulphur dioxide acting on the dithionate increases the yield of sulphate; and in a sealed tube at 200°, much sulphur dioxide and sulphate are produced by the decomposition of the dithionate. P. Berthier reported that silver sulphite is insoluble in water; J. S. Muspratt, that it is very slightly soluble; and

H. Baubigny, that water dissolves less than 0·05 grm. of silver sulphite. P. Berthier found that it is almost insoluble in sulphurous acid, but is soluble in aq. ammonia; H. Rose, that it forms soluble complex salts with alkali sulphites; A. Rosenheim, that alkali hydrosulphite soln. dissolve marked quantities of the sulphite; J. F. W. Herschel, that it is easily soluble in a soln. of alkali thiosulphate; P. Berthier, that strong acids—not acetic acid—displace sulphurous anhydride; J. Krutwig, that chlorine reacts: $2Ag_2SO_3+2Cl_2=4AgCl+2SO_2+O_2$; and C. W. B. Normand and A. C. Cumming, that iodine reacts: $Ag_2SO_3+I_2+H_2O=2AgI+H_2SO_4$. G. Bruno and G. Levi prepared **silver tetramminosulphite,** $Ag_2SO_3.4NH_3$; and N. Svensson, **sodium silver chlorosulphite,** $3Na_2SO_3.AgCl.21H_2O$, soluble in water. N. Steigmann found that soln. of the complex salt, with or without an excess of sodium sulphite, deposit a precipitate when kept several hours. The precipitate consists partly of silver sulphite, and partly of silver. The longer the soln. is kept, the higher the rates of silver in the precipitate. The autoreduction is strongly catalyzed by traces of a copper salt.

A. F. de Fourcroy and L. N. Vauquelin, and N. Svensson prepared **ammonium silver sulphite,** $(NH_4)AgSO_3.H_2O$, by dissolving silver sulphate in a soln. of ammonium sulphite, and evaporating the liquid over sulphuric acid. If the soln. be warmed, it decomposes. The yellowish-brown prisms are insoluble in water. N. Svensson, and A. Rosenheim and S. Steinhäuser prepared prismatic crystals of **ammonium silver heptasulphite,** $7(NH_4)_2SO_3.Ag_2SO_3.19H_2O$, by concentrating a soln. of freshly precipitated silver chloride in one of ammonium sulphite; and also from a soln. of silver sulphite in an excess of ammonium sulphite. A. Rosenheim and S. Steinhäuser also obtained **ammonium silver tetrahydroenneasulphite,** $4(NH_4)_2SO_3.4(NH_4)HSO_3.Ag_2SO_3.16H_2O$, which N. Svensson had previously obtained and represented by the formula, $3(NH_4)_2SO_3.4(NH_4)HSO_3.Ag_2SO_3.18H_2O$, in hygroscopic, quadratic crystals, from the mother-liquor obtained from the salt which precedes; from a soln. of silver chloride in one of ammonium sulphite and hydrosulphite. The salt is freely soluble in water, and the soln. decomposes when heated. The salt soon blackens in air, but not in contact with its mother-liquid. Prismatic crystals of **sodium silver sulphite,** $NaAgSO_3.H_2O$(or $2H_2O$), were obtained by N. Svensson from a sat. soln. of silver sulphite in a sat. soln. of sodium sulphite; and A. Rosenheim and S. Steinhäuser, by a similar process. The salt is decomposed by water. The last-named also obtained needles of **sodium silver tridecasulphite,** $12Na_2SO_3.Ag_2SO_3.84H_2O$, from a soln. of silver chloride in a sat. soln. of sodium sulphite. H. Baubigny obtained the same salt, and found that it slowly decomposed at ordinary temp. in darkness, and more rapidly in light—silver is formed. Water at 100° forms 97·5 per cent. of dithionate, and 2·5 per cent. of sulphate. A. Rosenheim and S. Steinhäuser could not prepare **potassium silver sulphite,** from a soln. of silver sulphite in one of potassium sulphite.

C. Winkler obtained colloidal gold by the action of auric chloride on a dil. soln. of sulphurous acid. A. Haase prepared **ammonium aurous sulphite,** $(NH_4)_3Au(SO_3)_2.1\frac{1}{2}H_2O$, from the mother-liquor of the amminosalt, and by treating barium aurous sulphite with a soln. of ammonium carbonate. The **ammonium aurous triamminodisulphite,** $(NH_4)Au_3(SO_3)_2.3NH_3.4H_2O$, according to A. Rosenheim and co-workers, or, according to A. Haase, $(NH_4)_2O.3Au_2O.4SO_2.6NH_3.3H_2O$, or $2(NH_4)_2O.5Au_2O.7SO_2.10NH_3.2H_2O$, was obtained by dropping a dil. soln. of auric chloride, as nearly neutral as possible, into a warm soln. of ammonium sulphite in conc. ammonia. The regular, six-sided plates are white, and are rapidly decomposed in moist air. The soln. in aq. ammonia is decomposed, when warmed, with the separation of gold. The salt is also decomposed by water and acids. A. Rosenheim and co-workers preferred to represent this salt as *ammonium aurosic tetrasulphite,* $Au_5'Au'''(SO_3)_4.8NH_3.6H_2O$. A. Haase prepared **sodium aurous disulphite,** $Na_3Au(SO_3)_2.1\frac{1}{2}H_2O$, by the action of a soln. of sodium carbonate on recently-precipitated barium aurous sulphite. It is also formed by dropping a soln. of auric chloride in a warm conc. soln. of sodium sulphite; by mixing sodium hydrosulphite with a warm alkaline soln. of sodium aurate; or by the action of sulphur dioxide on an alkaline soln. of sodium aurate at 40°–50°. Probably the same compound was described by C. Himly in 1846. The pale orange-coloured salt darkens when dried. The aq. soln. is gradually decomposed by air; but it is more stable in the presence of an excess of sodium sulphite, or sulphurous acid. It is precipitated by alcohol from these soln. It is decomposed by the stronger acids and gold is precipitated—both acetic and oxalic acids partially decompose the salt. Hydrogen sulphide gives a precipitate after acidification with hydrochloric acid. Salts of copper, calcium, strontium, magnesium, zinc, aluminium, iron(ic), cobalt, and nickel give no precipitate. It is soluble in rather less than its own weight of water, and is insoluble in alcohol. A. Rosenheim and co-workers regard the salt as a *sodium aurosic sulphite.* B. Oddo and Q. Mingoia prepared the salt, $Na_5Au(SO_3)_4.5H_2O$, by neutralizing an aq. soln. of auric chloride with sodium hydroxide, and adding sodium sulphite; the addition of alcohol to the filtrate precipitates the yellow salt which has a green fluorescence. The mol. wt. calculated from the lowering of the f.p. of water has one-eighth to one-tenth the theoretical value; so that the ionization is taken to be $Na_5Au(SO_3)_4 \rightleftharpoons 3SO_3'' + AuSO_3^{\cdot} + 5Na^{\cdot}$; and the structure of the $AuSO_3$-ion, $O : S = O_2 = Au$. The conductivity, μ, of soln. with M mols per litre at 18° is:

M .	0·0255	0·0140	0·0077	0·0034	0·0014	0·00021
μ . .	501	521	556	611	661·2	709·2

The anti-tubercular action is discussed by H. Mollgaard. The salt is completely absorbed from hypodermic or intramuscular injection, whilst there is a definite bactericidal action on Koch's bacillus, the antitubercular action is not so great. In man, the maximum tolerated dose is 0·1 to 0·2 grm. A. Haase prepared **potassium aurous disulphite,** possibly $K_3Au(SO_3)_2.nH_2O$, from the barium salt as in the case of sodium aurous disulphite.

A. Rosenheim and co-workers found that when a conc. soln. of auric chloride is added drop by drop to a soln. of ammonium sulphite, containing an excess of ammonia, and the soln. gently warmed, colourless, lustrous leaflets of **auric tetramminosulphite,** $Au_2(SO_3)_3(NH_3)_4.4H_2O$, separate. The salt is decomposed by moist air, and in neutral soln. They also prepared **sodium auric sulphite,** $5Na_2SO_3.Au_2(SO_3)_3.28H_2O$, by mixing a conc. soln. of auric chloride with sodium hydroxide, until the precipitate redissolves, and adding, drop by drop, a conc. soln. of sodium sulphite so long as the soln. remains alkaline. The pale yellow needles are washed successively with alcohol, and ether, and dried in air. The corresponding **potassium auric octosulphite,** $5K_2SO_3.Au_2(SO_3)_3.5H_2O$, was prepared in an analogous manner. E. Frémy obtained the salt, in yellow needles, by the action of potassium sulphite on a soln. of potassium aurate. It rapidly decomposes in neutral or acidic soln., but is stable in alkaline soln. Colourless needles of **potassium auric tetramminohexasulphite,** $3K_2SO_4.Au_2(SO_4)_3.4NH_3.4H_2O$, were obtained by mixing a soln. of auric chloride with a conc. ammoniacal soln. of potassium sulphite, and cooling the filtered liquid.

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§ 18. The Alkaline Earth Sulphites

J. S. Muspratt [1] obtained **calcium sulphite,** $CaSO_3.2H_2O$, by the action of alkali sulphites, or sulphurous acid, on a soln. of calcium hydroxide or chloride—K. Seubert and M. Elten recommended mixing 0·1*N*-soln. of calcium chloride and sodium sulphite, and obtained a precipitate free from basic salt. A. H. Röhrig passed sulphur dioxide into water in which calcium carbonate was suspended. The technical preparation of calcium sulphite was discussed by J. W. Kynaston, R. Powell, and A. Frank. F. R. Bichowsky prepared the dihydrate (1) by precipitation of fresh sodium bisulphite with calcium chloride, (2) by recrystallization of commercial calcium sulphite from a soln. of sulphurous acid, (3) by partial oxidation of calcium thiosulphate with hydrogen peroxide in alkaline soln. (a new reaction), (4) by thermal decomposition of soln. of calcium thiosulphate. The white, precipitated sulphite was found by J. S. Muspratt to be sparingly soluble in sulphurous acid, and the soln. furnishes six-sided prisms, with a sulphurous taste. A. H. Röhrig found that at 80° three-fourths of the water of crystallization is expelled, and all at 100°. F. Schott showed that at 125°, the precipitated sulphite loses almost 8·66 per cent. of water, and at a red-heat a variable amount of sulphur dioxide, so that the residue contains calcium oxide, sulphide, and sulphate. R. G. W. Farnell studied the precipitation of calcium sulphite in sugar factories. F. Förster and K. Kubel observed that calcium sulphite decomposes at 650°, $4CaSO_3 \rightleftharpoons 3CaSO_4 + CaS$, but above 900°, the equilibrium is disturbed by the reaction $CaSO_3 \rightleftharpoons CaO + SO_2$. This dissociation is perceptible at 650°, and is almost complete at 1100°. The residue contains calcium sulphate and oxide because the equilibrium $3SO_2 \rightleftharpoons 2SO_3 + S$ becomes effective at high temp. The rate of decomposition increases rapidly between 650° and 700°, but only slowly between 700° and 800°. F. R. Bichowsky gave 42·7 cals. per mol for the sp. ht. of $CaSO_3.2H_2O$; and for the heat of the reaction at 25°, $Ca + SO_3 + 2H_2O = CaSO_3.2H_2O + 9740$ cals. M. Trautz and S. Pakschwer found $(Ca, S_{rb}, 1\frac{1}{2}O_2, 2H_2O) - 284 \cdot 3$ Cals. ; and $CaSO_3.2H_2O + H_2O_2aq. = CaSO_4.2H_2O + H_2O + 81 \cdot 3$ Cals. The mixture of calcium sulphate and sulphide obtained by heating the sulphite to redness was found by A. Forster to be phosphorescent. J. S. Muspratt observed that the sulphite slowly oxidizes to sulphate in air ; 100 parts of cold water dissolve 0·125 part of salt. J. Robart showed that at 100°, a litre of water dissolves calcium sulphite eq. to 78 mgrm. of CaO ;

and a 12 per cent. soln. of sugar at the same temp. dissolves sulphite eq. to 37 mgrm. CaO. J. Weisberg found that a litre of a 10 per cent. soln. of sugar at 18° dissolves 0·0825 grm. of calcium sulphite, and 0·0800 grm. is dissolved by a 30 per cent. soln. of sugar at 18°. F. R. Bichowsky gave $0{\cdot}0_4372$ mols per litre at 25°. T. van der Linden found that the solubility of calcium sulphite in water and in sugar soln. is depressed by the presence of calcium sulphate from 0·065 to 0·032 grm. per litre; and also by raising the temp. E. C. Franklin and C. A. Kraus found that calcium sulphite is insoluble in liquid ammonia; W. Eidmann, and W. H. Krug and K. P. MacElroy, insoluble in acetone; and A. Naumann, insoluble in methyl or ethyl acetate. R. Wagner said that when oxidized by water and iodine, calcium iodide and sulphate are produced. L. Carius found a difficulty in obtaining a thoroughly dry sulphite, but by keeping the calcium salt in a current of dry air at 150°, he obtained the dry salt and found that in a sealed tube with phosphorus oxychloride at 120°, there is but a very slight reaction; at 150°, he did not observe the formation of thionyl chloride, but found that a reaction evolving large quantities of sulphur dioxide occurred, $3CaSO_3+2POCl_3=Ca_3(PO_4)_2+3SOCl_2$, but, according to E. Divers and T. Shimidzu: $6CaSO_3+2POCl_3=Ca_3(PO_4)_2+3CaCl_2+6SO_2$. If dry calcium oxide at 400° be treated with dry sulphur dioxide, for 60 hrs., K. Birnbaum and C. Wittich found that the product corresponds with **calcium oxypentasulphite,** $6CaO.5SO_2$. F. Schott added that at ordinary temp. very little sulphur dioxide is taken up; at a temp. higher than 400°, the product is a mixture of calcium sulphide, sulphite, and sulphate. E. F. Anthon added that at ordinary temp., calcium hydroxide is only about half neutralized by sulphur dioxide. The acid sulphite—**calcium hydrosulphite,** $Ca(HSO_3)_2$—is known only in soln. B. W. Gerland found that 100 c.c. of water with 9 grms. of sulphur dioxide in soln. dissolve 0·553 grm. of calcium sulphite. A similar soln. was obtained by J. von Liebig by dissolving calcium carbonate in sulphurous acid. The technical preparation of the acid sulphite soln. was discussed by J. W. Kynaston, O. Giller, D. W. Stewart, and R. Hasenclever. Sulphite liquors prepared from gases resulting from the combustion of sulphur or pyrites were shown by R. Sieber to contain thiosulphates and polythionates.

J. S. Muspratt obtained anhydrous **strontium sulphite,** $SrSO_3$, by adding an alkali sulphite to a soln. of a strontium salt. K. Seubert and W. Elten made it by mixing 0·1*N*-soln. of strontium nitrate and sodium sulphite, and added that the white precipitate supposed to be anhydrous is really the *hemihydrate*, $CaSO_3.\frac{1}{2}H_2O$, whether precipitated hot or cold. The white, tasteless powder can be crystallized from its soln. in sulphurous acid. J. S. Muspratt said that the sulphite slowly oxidizes in air to sulphate. W. Autenrieth and A. Windaus found that 100 grms. of water dissolve 0·0033 grm. of the salt. L. L. de Koninck found that the solubility in the presence of an excess of sodium sulphite is nearly the same as that of strontium sulphate in a soln. of ammonium sulphate.

A. F. de Fourcroy and L. N. Vauquelin passed sulphur dioxide into water with barium carbonate in suspension, or into an aq. soln. of a barium salt, and obtained **barium sulphite,** $BaSO_3$. K. Seubert and M. Elten, J. S. Muspratt, and A. Forster also made the same salt. It is obtained by mixing, say, normal soln. of sodium sulphite and barium chloride or nitrate. The white precipitate, said J. S. Muspratt, consists of tasteless, needle-like crystals; A. H. Röhrig said it dissolves easily—J. S. Muspratt said sparingly—in sulphurous acid, and the soln. was found by A. F. de Fourcroy and L. N. Vauquelin to furnish tetrahedral crystals. J. S. Muspratt found that the crystals decrepitate when warmed and give off when heated a little water, and sulphur and sulphur dioxide; while A. Forster observed that the mixture of sulphide and sulphate formed by heating the sulphite out of contact with air is phosphorescent; and P. Bary found that the uncalcined salt phosphoresces neither in Becquerel's rays nor in X-rays. V. J. Sihvonen found maxima in the ultra-red reflection spectrum at $10{\cdot}9\mu$ and $19{\cdot}7\mu$. A. F. de Fourcroy and L. N. Vauquelin found that barium sulphite is sparingly soluble in water; and, according to W. Autenrieth and A. Windaus, 100 grms. of water at ordinary temp. dissolve 0·00022 grm. of the salt. J. Rogowicz gave for the solubility, *S*, in water and in soln. of sucrose—*p* per cent. by weight—at 20° and 80°, in grams of barium sulphite per 100 c.c. of solvent :

p		0	10	20	30	40	50	60
S	20°	0·01974	0·01040	0·00968	0·00782	0·00484	0·00298	0·00223
	80°	0·00177	0·00335	0·00289	0·00223	0·00158	0·00149	0·00112

A. Naumann found barium sulphite to be insoluble in acetone, and in methyl acetate. C. St. Pierre found that the soln. in sulphurous acid is decomposed when heated out of contact with air, forming sulphuric acid, and a polythionic acid ; while W. Spring showed that sulphur monochloride converts it into a trithionate. A. Haase mixed a soln. of sodium aurous sulphite with barium chloride and obtained first a precipitate of barium sulphate, then barium sulphite. The filtrate was mixed with barium chloride, and an amorphous precipitate of **barium aurous sulphite,** $3BaSO_3.Au_2SO_3.nH_2O$, was formed which was converted by ammonium, sodium, or potassium carbonate into the corresponding aurous salt.

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§ 19. The Sulphites of the Beryllium-Mercury Family

According to P. Berthier,[1] beryllium hydroxide is readily soluble in sulphurous acid ; and H. Böttinger found that if aluminium hydroxide or ammonium sulphate be also present, boiling the soln. will re-precipitate the beryllium hydroxide. G. Krüss and H. Moraht obtained normal **beryllium sulphite,** $BeSO_3$, by allowing absolute alcohol, saturated with sulphur dioxide, to act on freshly precipitated beryllium hydroxide well-washed with alcohol. The colourless soln. was evaporated in vacuo. The white crystalline powder consists of hexagonal plates which are stable in dry air. They are very hygroscopic, and in moist air form the basic sulphite. The salt is hydrolyzed by water. A. Atterberg obtained **beryllium oxysulphite,** $BeO.BeSO_3$, by adding alcohol to a soln. of beryllium hydroxide in sulphurous acid, and the thick syrupy precipitate crystallizes when confined over conc. sulphuric acid. G. Krüss and H. Moraht obtained **beryllium oxytrisulphite,**

$BeO.3BeSO_3$, by evaporating in vacuo a soln. of the oxysulphite in absolute alcohol to which a few drops of sulphurous acid have been added. K. Seubert and M. Elten obtained the **beryllium octohydroxydisulphite,** $8Be(OH)_2.2BeSO_3.6H_2O$, by mixing at ordinary temp. normal soln. of beryllium chloride and sodium sulphite. It is probable that these basic salts are arbitrary stages in hydrolysis of the normal sulphite. According to A. Rosenheim and P. Woge, crystals of **potassium beryllium trisulphite,** $K_2SO_3.2BeSO_3.9H_2O$, are produced by evaporating, in an atm. of sulphur dioxide, a soln. of beryllium hydroxide and freshly prepared potassium hydrosulphite in sulphurous acid. They also obtained a precipitate of **ammonium beryllium sulphite,** $(NH_4)_2O.2BeO.3SO_2.4H_2O$, which was very unstable in air.

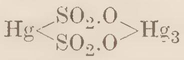
P. J. Hartog [2] obtained anhydrous **magnesium sulphite,** $MgSO_3$, by dehydrating one of the hydrates at 170° in a current of dry hydrogen—not sulphur dioxide. A. H. Röhrig, E. Mitscherlich, and J. S. Muspratt obtained the *trihydrate*, $MgSO_3.3H_2O$, by crystallization from hot soln., or by crystallization over sulphuric acid; and P. J. Hartog, the *hexahydrate*, $MgSO_3.6H_2O$, by evaporating the soln. below 100° in vacuo. The aq. soln. was made by P. J. Hartog, G. A. Archbold, and R. H. Davies by passing sulphur dioxide through water with magnesia, or *magnesia alba* in suspension, and evaporating the filtered soln. C. G. Schwalbe and K. Berndt described the preparation of magnesium hydrosulphite liquors for cellulose. K. Seubert and M. Elten obtained the hexahydrate by crystallization at ordinary temp. from a soln. of $0{\cdot}1N$-$MgSO_4$ and $0{\cdot}1N$-Na_2SO_3. The trihydrate forms transparent rhombic crystals; the crystals of the hexahydrate are trigonal pyramids which G. Werther found to have the axial ratio $a:c=1:1{\cdot}0296$. C. F. Wittich found that the salt begins to decompose: $5MgSO_3=2MgSO_4+3MgO+2SO_2+S$ about 210°–215°. F. Förster and K. Kubel said that magnesium sulphite at 300° decomposes according to $4MgSO_3=(2MgSO_4+2MgSO_2)=2MgSO_4+MgS_2O_3+MgO$, where the magnesium sulphoxylate is an intermediate product. The partial decomposition of the thiosulphate: $MgS_2O_3=MgSO_3+S$, and the dissociation of the sulphite: $MgSO_3\rightleftharpoons MgO+SO_2$, occur at higher temp. P. J. Hartog gave for the heat of formation: $(Mg,S,3O)=222{\cdot}92$ Cals.; $(MgSO_3,3H_2O_{solid})=11{\cdot}4$ Cals.; and $(MgSO_3.6H_2O_{solid})=13{\cdot}88$ Cals. A. F. de Fourcroy and L. N. Vauquelin said that the taste of the salt is earthy and then sulphurous, and when heated the salt loses water and then sulphur dioxide; in air the crystals become opaque, forming magnesium sulphate; and 100 parts of cold water dissolve 5 parts of salt; hot water dissolves more salt; H. Hager said that 100 parts of cold water dissolve 1·25 parts of salt; and boiling water, 0·833 part. K. Seubert and M. Elten showed that when magnesium sulphite is crystallized from hot water, no basic salt is produced; G. A. Barbaglia and P. Gucci, that when heated in a sealed tube with sulphurous acid: $3Mg(HSO_3)_2=3MgSO_4+H_2SO_4+2S+2H_2O$; E. C. Franklin and C. A. Kraus, that it is insoluble in liquid ammonia; and is precipitated from its aq. soln. by alcohol. The acid salt **magnesium hydrosulphite,** $Mg(HSO_3)_2$, is known only in aq. soln. A. F. de Fourcroy and L. N. Vauquelin obtained **ammonium magnesium sulphite,** $(NH_4)_2SO_3.3MgSO_3.18H_2O$, from a soln. of magnesia in one of ammonium sulphite; C. F. Rammelsberg, from a soln. of its component salts; and P. J. Hartog, by neutralizing a soln. of magnesium sulphite with ammonia, passing sulphur dioxide into the soln.; and again neutralizing with ammonia. The crystals were obtained by evaporating the soln. in vacuo. A. F. de Fourcroy and L. N. Vauquelin found that the crystals are almost tasteless, and are sparingly soluble in water. J. C. G. de Marignac gave for the axial ratios of the monoclinic prisms $a:b:c=1{\cdot}9612:1:0{\cdot}8741$, and $\beta=125°\ 18'$. The (100)-cleavage is distinct. P. J. Hartog found that the crystals lose 12 mols. of water at 115°–120°; and decompose above 125°. The heat of formation is $(3MgSO_3.6H_2O,(NH_4)_2SO_3)=-2{\cdot}110$ Cals.; $(3MgSO_3,(NH_4)_2SO_3,18H_2O_{solid})=39{\cdot}48$ Cals.; and $(3MgSO_3,(NH_4)_2SO_3,6H_2O_{solid})=26{\cdot}18$ Cals. F. L. Hahn obtained the complex salt as in the case of the ammonium copper sulphite.

A. F. de Fourcroy and L. N. Vauquelin [3] dissolved zinc oxide in sulphurous acid, and obtained small crystals which, according to the analyses of J. S. Muspratt, and M. J. Fordos and A. Gélis, are *dihydrated* **zinc sulphite,** $ZnSO_3.2H_2O$, and, according to those of C. F. Rammelsberg, J. C. G. de Marignac, and G. Denigès, are the *hemipentahydrate*, $ZnSO_3.2\frac{1}{2}H_2O$. A. Vogel obtained the crystals by evaporating the aq. soln.; J. S. Muspratt, by precipitating with alcohol or ether; and P. Berthier, and K. Seubert showed that if the soln. be boiled, a basic salt is formed. G. Denigès mixed a cold soln. of 100 grms. of zinc sulphate and 400 grms. of water and 2 c.c. of acetic acid, with one of 100 grms. of sodium sulphite, 400 grms. of water and 2 c.c. of acetic acid; and K. Seubert and M. Elten, cold normal soln. of zinc sulphate and sodium sulphite.

The prismatic or acicular crystals were found by J. C. G. de Marignac to be monoclinic with the axial ratios $a:b:c=0\cdot836:1:0\cdot821$, and $\beta=93°\ 40'$. F. T. Heuston and C. R. C. Tichborne said that when dried at 100°, the crystals are dehydrated; while K. Seubert said that the salt with $2\frac{1}{2}$ mols. of water loses all the water at 100°. A. H. Röhrig obtained the *monohydrate* by pressing the dihydrate between bibulous paper for a long time. C. F. Rammelsberg found that at 200°, sulphur dioxide is evolved and the residual zinc oxide contains some sulphate. A. F. de Fourcroy and L. N. Vauquelin said that the salt is sparingly soluble in water, and insoluble in alcohol; and C. J. Koene, that it is sparingly soluble in sulphurous acid, without forming **zinc hydrosulphite,** $Zn(HSO_3)_2$. W. E. Henderson and H. B. Weiser observed that when zinc sulphite is precipitated by passing sulphur dioxide into water with zinc sulphide in suspension, the zinc sulphite first precipitated passes into soln. as the hydrosulphite—*vide infra*, manganese and ferrous sulphites. According to M. Michels, zinc sulphite absorbs basic dyes at 100° but not in the cold. C. F. Rammelsberg observed that the soln. in aq. ammonia, when evaporated in a warm place, deposits crystals of **zinc amminosulphite,** $ZnSO_3.NH_3$; M. Prud'homme showed that the soln. of zinc in ammonium hydrosulphite gives **zinc diamminosulphite,** $ZnSO_3.2NH_3$. F. Ephraim and E. Bolle obtained **zinc triamminosulphite,** $ZnSO_3.3NH_3.nH_2O$, by saturating a soln. of the sulphite with ammonia. C. Brückner showed that when zinc sulphite soln. is reduced with magnesium, sulphur dioxide, and zinc oxide, sulphide, and sulphate are formed; the Badische Anilin- und Sodafabrik, that with zinc-dust and formaldehyde, a complex compound of formaldehyde and zinc hydrosulphite is formed; and G. Scurati-Manzoni, that boiling with manganous hyroxide forms zinc hydroxide and manganese sulphate. P. Ray and B. K. Goswami added a soln. of zinc hydrosulphite to an excess of a conc. soln. of hydrazine, and dried the voluminous, white precipitate of **zinc dihydrazinosulphite,** $ZnSO_3.2N_2H_4.1\frac{1}{2}H_2O$, over sulphuric acid in vacuo. The salt is alkaline towards litmus, and it is decomposed by water. If a suspension of this salt in water is treated with sulphur dioxide, **zinc hydrazinohydrosulphite,** $Zn(HSO_3)_2.N_2H_4$, is formed as a white powder which is acidic towards litmus. If a soln. of zinc hydrosulphite is added to a dil. soln. of hydrazine acetate, or hydrate, a mixture of this salt and zinc sulphite is formed. K. Seubert reported that the basic salt **zinc octoxypentasulphite,** $8ZnO.5ZnSO_3.4H_2O$, or $8Zn(OH)_2.5ZnSO_3$, is obtained from a warm soln. of $0\cdot1N$-$ZnSO_4$ and $0\cdot1N$-Na_2SO_3; or by heating a dil. soln. of zinc sulphite, or diluting a conc. soln.; and *zinc heptoxyoctosulphite*, $7ZnO.8ZnSO_3.nH_2O$, or $7Zn(OH)_2.8ZnSO_3.7H_2O$, or possibly **zinc dihydroxysulphite,** $Zn(OH)_2.ZnSO_3.H_2O$, by mixing warm normal soln. of zinc sulphate and sodium sulphite. E. Berglund obtained **ammonium zinc sulphite,** $(NH_4)_2SO_3.ZnSO_3$, from a soln. of zinc chloride and ammonium chloride with an excess of ammonia and neutralized with sulphur dioxide. F. L. Hahn and co-workers prepared the ammonium zinc sulphite as in the case of the ammonium copper sulphite. Unstable white crystals of **potassium zinc sulphite,** $K_2SO_3.3ZnSO_3.7\frac{1}{2}H_2O$, were obtained in an analogous way. The salt is decomposed by water.

M. J. Fordos and A. Gélis found that when cadmium dissolves in sulphurous acid, cadmium sulphide and sulphite are formed. C. F. Rammelsberg obtained anhydrous **cadmium sulphite,** $CdSO_3$, by passing sulphur dioxide through water with cadmium carbonate in suspension ; and evaporating the liquid. A. H. Röhrig evaporated a soln. of cadmium carbonate in sulphurous acid. G. Denigès obtained the *trihydrate,* $CdSO_3.3H_2O$, from a cold, dil. acetic acid soln. of cadmium sulphate in $2\frac{1}{2}$ times its weight of water and a similar soln. of sodium sulphite ; if boiling soln. be used, the anhydrous salt is obtained. J. S. Muspratt obtained the *dihydrate,* $CdSO_3.2H_2O$, by precipitating the aq. soln. with alcohol ; and K. Seubert and M. Elten, as a granular precipitate, from a soln. corresponding with $3CdSO_4.8H_2O+3Na_2SO_3=3CdSO_3+3Na_2SO_4+8H_2O$; G. Denigès, the *hemitrihydrate,* $CdSO_3.1\frac{1}{2}H_2O$, by mixing 10 per cent. soln. of cadmium nitrate and sodium sulphite ; and K. Seubert and M. Elten used *N*-soln. of cadmium sulphate and sodium sulphite ; C. F. Rammelsberg found that the salt is slowly oxidized in air ; and when heated, it forms a mixture of cadmium oxide, sulphide, and sulphate. It dissolves sparingly in water, and freely in dil. acids. J. S. Muspratt said that the salt is soluble in aq. ammonia, and insoluble in alcohol ; and A. Naumann, insoluble in acetone. C. F. Rammelsberg found that when the soln. in aq. ammonia is cooled, it furnishes **cadmium amminosulphite,** $CdSO_3.NH_3$, as a crystalline powder. P. Ray and B. K. Goswami prepared **cadmium hydrazinosulphite,** $CdSO_3.N_2H_4$, as in the case of the zinc dihydrazinosulphite, and **cadmium hydrazinohydrosulphite,** as in the case of the corresponding zinc salt. E. Schüler passed sulphur dioxide into a soln. of cadmium chloride saturated with ammonia, and obtained a white, crystalline precipitate of **ammonium cadmium sulphite,** $CdSO_3.(NH_4)_2SO_3$. F. L. Hahn and co-workers prepared the complex salt as in the case of the ammonium copper sulphite. E. Berglund obtained **sodium cadmium sulphite,** $Na_2SO_3.3CdSO_3$, or $(Na.O.SO.O.Cd.O.SO.O)_2Cd$, as a white crystalline powder, by adding sodium sulphite to a soln. of a cadmium salt until the precipitate first formed redissolves, and allowing the liquid to stand for crystallization ; he could not prepare **potassium cadmium sulphite.**

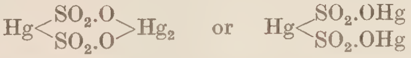
A. Vogel[4] supposed that he had made white **mercurous sulphite,** Hg_2SO_3, by the action of an excess of sulphurous acid on mercuric oxide ; and C. F. Rammelsberg, a basic sulphate, $Hg_2O : SO_2=2 : 3$ or $3 : 4$, by passing sulphur dioxide into water with freshly precipitated mercuric oxide in suspension. L. P. de St. Gilles said that the soln. produced in the action of sulphur dioxide on mercuric oxide suspended in water yields a precipitate which is a mixture of mercurous and mercuric sulphites, and until this precipitate had formed, the soln. did not contain either a mercurous salt or a sulphate. K. Seubert and M. Elten, and E. Divers and T. Shimidzu were unable to prepare this salt. E. Divers and T. Shimidzu said that when mercurous sulphite might be expected to appear there is formed instead a metameric salt which he called *hypomercurosomercuric sulphite,* or **hypomercurosic sulphite,** $Hg_4(SO_3)_2.H_2O$, and represented by the formula :



$$Hg{<}\begin{matrix}SO_2.O\\SO_2.O\end{matrix}{>}Hg_3$$

where Hg_3 is regarded as a bivalent mercurous radicle in the same sense that Hg_2 is the bivalent mercurous radicle. Oxymercurous salts are blackened by sulphurous acid and the sulphites, as A. Vogel noticed when he treated mercurous nitrate with sulphurous acid, he mistook the resulting black powder for mercury itself, whereas E. Divers and T. Shimidzu showed that the product is really hypomercurous sulphite. This compound is formed in the reaction between sulphurous acid, water, and mercurosic sulphate, mercuric oxysulphite, and mercurous sulphate or nitrate : mercurosic sulphite, mercuric oxysulphite, and mercurous sulphate or nitrate : $2(H.SO_3H)+2(HgNO_3)_2=4HNO_3+Hg(SO_3)_2.Hg_3$. It is also formed by the action of a soln. of sodium sulphite on mercuric oxysulphite, mercurosic sulphite, and mercurous sulphate, nitrate, or chloride : $2Na(SO_2.ONa)+2(HgNO_3)_2=4NaNO_3+Hg(SO_2O)_2Hg_3$; and by the action of silver sulphite on an aq. soln. of mercurous nitrate or sulphate. Mercurosic hyposulphite is a greyish-black amorphous substance, obtained as a voluminous, flocculent precipitate, insoluble in water. It is very unstable in water, but can be preserved dry for a considerable time, without much change. Left to itself at common temp., it very slowly evolves sulphur dioxide, leaving mercurous sulphate and mercury. The co-operation of moisture is, no doubt, essential to this change, the primary form of which will be hydrolysis into mercury and sulphuric acid, to be followed by reaction between unchanged sulphite and the sulphuric acid. The production of sulphur dioxide and mercury shows the change not to be one of oxidation of sulphite to sulphate by the air: $Hg_4(SO_3)_2.H_2O=2Hg+Hg_2SO_4+SO_2+H_2O$. Heated dry to 80°, it rapidly undergoes a change similar to that which takes place slowly in air. When gradually heated in vacuo, the liberated mercury is volatilized. When heated with sufficient water there is a tumultuous reaction: $Hg_4(SO_3)_2.H_2O+H_2O=4Hg+2H_2SO_4$. If the proportion of water is so small as to leave the sulphuric acid somewhat concentrated, some mercurous sulphate is also formed, but not otherwise. The product of the sulphate is then due to a reaction between unchanged sulphate and the sulphuric acid. Hypomercurosic sulphite resists the action of rather dil. sulphuric acid. It is converted by a soln. of potassium hydroxide into mercuric potassium sulphite, which dissolves, and mercurous oxide and mercury which remain insoluble: $Hg(SO_2O)_2Hg_3.H_2O+2KOH=Hg(SO_2.OK)_2.H_2O+Hg+Hg_2O+H_2O$. Hydrochloric acid at once liberates sulphur dioxide, and forms mercuric chloride in some quantity. The insoluble matter only slowly changes from the nearly black colour of the sulphite to a light grey, even with thorough trituration of the whole in a mortar. It then consists of mercurous chloride and a very little free mercury, while the soln. contains no more than minute quantities of mercuric chloride. The primary reaction is: $Hg(SO_3)_2Hg_3+4HCl=HgCl_2+2H_2SO_3+Hg+Hg_2Cl_2$. The mercury and the mercuric chloride then slowly unite and form more mercurous chloride, as they can be shown experimentally to have the power to do. Possibly a black hypomercurous chloride, Hg_3Cl_2, is one of the primary products, which then acts upon the mercuric chloride: $Hg_3Cl_2+HgCl_2=2(HgCl)_2$. Dil. nitric and sulphuric acids have no action; and nitric acid reacts only when sufficiently concentrated to oxidize. Its resistance to acids is remarkable and distinguishes this compound from mercurous oxide. Sulphurous acid decomposes it, producing mercury and a soln. of mercuric hydrosulphite: $Hg(SO_3)_2Hg_3+2H(HSO_3)=2Hg+2Hg(HSO_3)_2$. The presence of sulphuric acid inhibits the action of sulphurous acid on hypomercurosic sulphite—otherwise it could not be possible to prepare the salt in a state of purity. A soln. of sodium sulphite converts hypomercurosic sulphite into mercuric sodium sulphite, and a residue of mercury, the action being similar to that of sulphurous acid. Silver sodium sulphite soln. takes mercury in place of its silver, all the silver being precipitated, if not in excess. The blackish hypomercurosic sulphite is converted into something still blacker, probably mercuric argentous sulphite. Excess of silver sodium sulphite does not destroy this black matter, or only slowly destroys it. If boiled with water, it yields spongy silver amalgam; and when washed with cold water, it slowly undergoes the same change. The reaction is perhaps: $Hg(SO_3)_2Hg_3+6Ag(SO_3Na)=Hg(SO_3)_2Ag_4+2Ag+3Hg(SO_3Na)_2$. If the silver sodium sulphite is used in excess, and after the reaction, it is diluted with water, it shows a greyish-white turbidity, through the liberation of a minute quantity of silver. Apparently a very little mercuric argentous sulphite dissolves in the undiluted soln. of the other sulphites, and on dilution parts with some of its silver. Sodium chloride soln. produces mercurous chloride, mercuric sodium sulphite, and mercury: $Hg(SO_3)_2Hg_3+2NaCl=Hg(SO_3Na)_2+Hg+(HgCl)_2$. Potassium iodide soln. converts it into mercurous iodide and potassium sulphite. Then, as in any case would happen, concentrated soln. of potassium iodide resolves this mercurous iodide into mercury, and mercuric iodide dissolving as double iodide; but the presence of the potassium sulphite does not appear to affect this decomposition of the mercurous iodide. Mercuric chloride soln. reacts with hypomercurosic sulphite to form mercurous chloride and sulphuric acid: $Hg_4(SO_3)_2+2H_2O+4HgCl_2 =2SO_4H_2+4(HgCl)_2$, but its action takes some time to complete, and the mercurous chloride is at first very grey. When the mercuric chloride is not in excess, the filtered soln. of sulphuric acid is free from both mercury and chlorine, but when it is added quickly in excess and at once filtered, a soln. is obtained which continues to deposit crystalline mercurous chloride for some time. The reaction is, therefore, similar to that between mercurosic sulphite and mercuric chloride. First, mercuric sulphite (or chloride-sulphite) and hypomercurous chloride (or mercury and mercurous chloride) are formed: $Hg(SO_3)_2Hg_3 + HgCl_2 = Hg(SO_3)_2Hg +Hg_3Cl_2(?Hg+Hg_2Cl_2)$; then mercuric sulphite and water become mercurosic sulphite and sulphuric acid; the mercurosic sulphite decomposes to form mercuric chloride; and so the changes follow on until no more sulphite remains. The hypomercurous chloride (or mercury) slowly unites with mercuric chloride to form mercurous chloride. Mercuric oxide (precipitated) has no immediate action on moist hypomercurosic sulphite. With the oxide not in excess, the mixture slowly changes to mercurous sulphate and mercury, a result apparently not due to any direct reaction between the two substances. With the oxide in excess, a bright orange-brown mercury oxysulphite is at once formed. It is at once decomposed by hydrochloric acid in the usual way, but is insoluble in dil. nitric acid; this affords a ready means of removing the excess of mercuric oxide. A little mercurous sulphate was present with it. Mercuric nitrate soln. rapidly converts hypomercurosic sulphite into mercurosic sulphite, becoming itself changed to mercurous nitrate: $Hg(SO_3)_2Hg_3+Hg(NO_3)_2=Hg(SO_3)_2Hg_2+(HgNO_3)_2$. As mercuric nitrate readily takes up mercury, the above equation, showing the transfer of one of the three atoms of the hypomercurous radicle to the mercuric nitrate, presents no difficulty. The mercurosic sulphite obtained in this way is always of a light buff colour, instead of white. This colour is characteristic of mercurosic sulphite not obtained by hydrolytic decomposition; for the reaction between mercuric sodium sulphite and mercurous nitrate or sulphate yields it also of this colour. Formed by hydrolytic methods, it is always exceedingly white. Mercuric sulphate soln. behaves like mercuric nitrate, but in this case the mercurous sulphate formed precipitates and mixes with the mercurosic sulphite. Mercurous nitrate soln. and mercurous sulphate are, as might be expected, inactive. So, too, is silver nitrate.

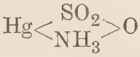
E. Paterno and U. Alvisi obtained **mercurosic sulphite,** $Hg_2SO_3.HgSO_3.nH_2O$, as a white precipitate, by the action of sulphur dioxide on a soln. of mercuric fluoride in dil. hydrofluoric acid. A yellow colour is possibly due to admixed mercury. E. Divers and T. Shimidzu represented this salt by the formula:



$$Hg{<}\begin{matrix}SO_2.O\\SO_2.O\end{matrix}{>}Hg_2 \quad \text{or} \quad Hg{<}\begin{matrix}SO_2.OHg\\SO_2.OHg\end{matrix}$$

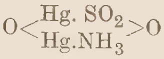
They obtained it as a *tetrahydrate,* by the action of sulphurous acid and water on mercuric oxide, oxysulphite, oxysulphate, sulphate, or nitrate; by the action of mercuric sodium sulphite and either dil. nitric acid or dil. sulphuric acid; of soln. of sodium sulphite on mercuric sodium sulphite or mercuric nitrate or sulphate; of a warm soln. of mercuric sodium sulphite on mercuric oxide; of mercuric sodium sulphite and mercurous sulphate or nitrate; and of hypomercurosic sulphite on mercuric nitrate or sulphate. Mercurosic sulphite is obtained in somewhat different states. Prepared by adding mercuric oxide to sulphurous acid soln., it is in lustrous, crystalline particles, which form felted sheets like paper, when drained on a tile till dry. Prepared from a paste of mercuric oxide and gaseous sulphur dioxide, it is not visibly crystalline, but it forms a voluminous precipitate of crystalline habit, is brilliantly white, and, when pressed whilst moist, crepitates like starch. Prepared by reaction between another mercury sulphite and a mercury nitrate or sulphate, it is a voluminous, apparently amorphous precipitate, of a buff colour. It is then not quite pure, indeed, but its colour can hardly be referred to the presence of any coloured impurity. Mercurosic sulphite is very efflorescent, and becomes anhydrous in the desiccator; only when crystalline can it be dried with all its water of crystallization retained. C. F. Rammelsberg found his red, crystalline cuprosic sulphite retained 2 mols. of water of crystallization; and L. P. de St. Gilles, the yellow amorphous cuprosic sulphite, 5 mols. The tetrahydrate may be a pentahydrate slightly effloresced. Mercurosic sulphite is insoluble in water. Mercurosic sulphite is so stable when dry as to be but very little changed after long keeping. In a closed vessel, it gradually darkens in colour, but nearly bleaches again on exposure to the air for some time. The darkening is in all probability due to the formation of a little hypomercurosic sulphite. Slowly in the air, more quickly in vacuo, it acquires a slight permanent grey colour, due to the presence of a minute quantity of mercury. The slow decomposition of mercurosic sulphate results in the production of mercurous sulphate, metallic mercury, sulphur dioxide, and water, the same products as those produced by heat. Sulphurous acid blackens both mercurous sulphate and mercurosic sulphite by forming hypomercurosic sulphite. After blackening and bleaching in the air, the changed sulphite may be somewhat buff-coloured. Heated dry at about 80°, it evolves sulphur dioxide, mercury, and water, and becomes at first black, then grey-white, leaving mercurous sulphate and some of the mercury as a residue; these may be separated by further heating, so as to volatilize the mercury. The blackening may certainly be referred to the formation of hypomercurosic sulphite, and although it is for the time very great, it is only transitory if the heat is maintained. Examined when blackest, the amount of undecomposed sulphite is exceedingly small. It is probable that hypomercurosic sulphite forms an intermediate product in the decomposition of the mercurosic sulphite; the moist sulphur dioxide no doubt produces it by a secondary action on the undecomposed mercurosic sulphite, or on the mercurous sulphate: $Hg_3(SO_3)_2+2H_2O=3Hg+2SO_4H_2$; $Hg+Hg_3(SO_3)_2+2SO_4H_2=2Hg_2SO_4+2SO_2+2OH_2$. When mercurosic sulphite is heated with water, it is converted tumultuously into metal and sulphuric acid. Enough water being present, no mercurous sulphate is produced: $Hg_3(SO_3)_2+2H_2O=3Hg+2SO_4H_2$. When the salt is heated dry, its decomposition begins in all probability in this way, but is then modified by the reaction between the sulphuric acid and unchanged sulphite, giving mercurous sulphate and sulphurous acid. The non-production of any mercuric sulphate is to be expected, as it is easy to show experimentally the instant conversion of mercuric sulphate to mercurous sulphate by moist mercury. Potassium hydroxide converts it into mercurous oxide, insoluble, and mercuric potassium sulphite, going into soln.: $Hg(SO_3)_2Hg_2+2KOH=H_2O+OHg_2+Hg(SO_3K)_2$, the potassium displacing the mercurous but leaving the mercuric radicle. Hydrochloric acid at once decomposes it, the products being sulphurous acid and the two chlorides of mercury. When the mercurosic sulphite is buff-coloured, the mercurous chloride from it is of the same colour. No sulphuric acid is produced in this reaction. The preparations of buff-coloured sulphite, however, to start with, always contain a small quantity of sulphate. Nitric acid and sulphuric acid in the dil. state are without action on mercurosic sulphite. More conc. acids dissolve it, but the nitric acid scarcely so unless it is concentrated enough to oxidize the sulphite. Sulphurous acid blackens and decomposes it, dissolving out the elements of mercuric sulphite and leaving hypomercurosic sulphite insoluble for a time, but then also decomposing. The presence of sulphuric or nitric acid greatly hinders, and for a time at least altogether prevents the action of the sulphurous acid, a circumstance greatly facilitating the preparation of mercurosic sulphite. The reaction between sulphurous acid and mercurosic sulphite in absence of sulphuric acid, consists in the exchange of non-oxylic hydrogen for oxylic mercury, as expressed in the following equation: $2Hg(SO_3)_2Hg_2+2H(SO_3H)=Hg(SO_3)_2Hg_3+2Hg(SO_3H)_2$. Sodium sulphite soln. produces effects similar to those of sulphurous acid, but acts more rapidly than the acid. The mercurosic sulphite is blackened by being converted into insoluble hypomercurosic sulphite, and mercuric sodium sulphite which dissolves; here also, as with sulphurous acid, the sodium sulphite exchanges its non-oxylic sodium for half the mercury of the oxylic mercurous radicle of the mercurosic sulphite, the other half of this mercury going to form hypomercurosic sulphite with mercurosic sulphite: $2Hg(SO_3)_2Hg_2+2Na(SO_3Na)=Hg(SO_3)_2Hg_3+2Hg(SO_3Na)_2$. The hypomercurosic sulphite thus formed is acted on by more sodium sulphite, becoming mercuric sodium sulphite and free mercury. Silver sodium sulphite soln. yields mercuric sodium sulphite in soln., all the silver being precipitated if not in excess. The insoluble sulphite is very black, and appears to be a mercury silver sulphite; it is too black for hypomercurosic sulphite, even unmixed with white silver sulphite; besides, hypomercurosic sulphite at once reacts with silver sodium sulphite. The reaction between the silver sodium sulphite and mercurosic sulphite appears, then, to be: $Hg(SO_3)_2Hg_2+4Ag(SO_3Na)=Hg(SO_3)_2Ag_4+2Hg(SO_3Na)_2$, in which mercuric argentous sulphite appears. Sodium chloride soln. added freely produces much black hypomercurosic sulphite, which slowly disappears on digestion. By adding the sodium chloride gradually, hypomercurosic sulphite is only produced by the first portions. This difference is due to the mercury salts which go into soln. by the action of the first portions modifying that of those added afterwards. The final result of the addition of sodium chloride is expressed by: $Hg(SO_3)_2Hg_2+2NaCl=Hg(SO_3Na)_2+(HgCl)_2$, but the primary action appears to be that of an exchange of sodium for the oxylic mercury, in which only half of this mercury combines with the chlorine, the other half then going to unite with more mercurosic sulphite: $2Hg(SO_3)_2Hg_2+4NaCl=Hg(SO_3Na)_2+Hg(SO_3)_2Hg_3+HgCl_4Na_2$. Then, as the quantity of mercuric chloride increases, and the mercurosic sulphite becomes less, all the mercury goes to form mercurous chloride, while any hypomercurosic sulphite previously formed is slowly converted into chloride. Mercuric sodium chloride acts in the same way as sodium chloride, the mercuric chloride taking no part; it has no action of its own on mercurosic sulphite, but when sodium chloride is present this salt acts first. Mercuric chloride soln. added, not in excess, produces mercurous chloride and sulphuric acid, all the mercury being precipitated: $Hg_3(SO_3)_2+2H_2O+3HgCl_2=3(HgCl)_2+2SO_4H_2$; but if added at once in excess, much mercuric sulphite goes into solution in the mercuric chloride, and then slowly changes to mercurous chloride and sulphuric acid, as already described under normal mercuric sulphite. Potassium iodide soln. forms a brownish-yellow mercury iodide and a soln. of mercuric potassium sulphite. Mercuric iodide, oxide, nitrate, and sulphate, and mercurous nitrate and sulphate, are without action.

According to L. P. de St. Gilles, normal **mercuric sulphite,** $HgSO_3$, separates as a white, curdy precipitate when a syrupy soln. of mercuric nitrate, free from an excess of nitric acid, is treated with a dil. soln. of sodium sulphite. He added that either the normal salt or a basic salt can be obtained according as the mercuric nitrate employed happens to be more or less basic. E. Divers and T. Shimidzu could not verify these statements. They found that whenever it might be supposed that mercuric sulphite would be formed by direct double decomposition, it does one of three things, according to circumstances; it forms with another basylous radicle a double sulphite such as mercuric sodium sulphite or mercuric hydrogen sulphite; it forms a basic sulphite or an oxysulphite with oxide of mercury taken from the nitrate or other mercuric salt; or it forms mercuroso-mercuric sulphite by suffering partial hydrolysis into sulphuric acid and its mercury element. They found that when normal mercuric nitrate, in the presence of that very small amount of nitric acid which seems to be essential to its existence even in conc. soln., is treated with a soln. of normal sodium sulphite, mercuric oxysulphite is, from the first, precipitated in a pure or nearly pure condition, and, as a consequence, the mother-liquor proves to be much more acid than the original nitrate soln. The accumulation of this free acid soon prevents the precipitation of more oxysulphite, while much mercuric nitrate yet remains in soln. The addition of more sodium sulphite is now followed by momentary effervescence of sulphur dioxide, and a partial blackening of the white precipitate. This blackening effect was observed by L. P. de St. Gilles, and he has given, as conditions of successful preparation of the sulphite and of the oxysulphite, avoidance of excess of the precipitant and the employment of the nitrate soln. in the conc. state and the sulphite soln. in the dil. state. But when some blackening has taken place, it soon disappears on agitating the precipitate with the mother-liquor, and, indeed, the mother-liquor may now be used to furnish more precipitate which, black at first, soon becomes white, provided too much sodium sulphite is not added. This white precipitate, however, consists not of the oxysulphite, but of another salt, mercurosic sulphite. The substitution of mercuric sulphate for the nitrate, or of silver sulphite for sodium sulphite, gives a similar result. Sodium sulphite and mercuric chloride furnish sodium mercuric sulphite. Silver sulphite and mercuric chloride react: $2Ag_2SO_3+3HgCl_2=4AgCl+Hg(SO_2O.HgCl)_2$; and the end-products of the reaction are: $Ag_2SO_3+H_2O+2HgCl_2=2AgCl+Hg_2Cl_2+H_2SO_4$. Mercurosic sulphite and mercuric chloride interact: $Hg(SO_2.O)_2Hg_2+HgCl_2=Hg_2Cl_2+Hg(SO_2.O)_2Hg$, and the mercuric sulphite is then hydrated to mercurosic sulphite: $3Hg(SO_3)_2Hg+2H_2O=2H_2SO_4+2Hg(SO_3)_2Hg_2$. Hypomercurosic sulphite behaves similarly. The action of sulphurous acid on mercuric oxide gives mercurosic sulphite; and the same product is obtained when dil. nitric or sulphuric acid acts on sodium mercuric sulphite. Hence, mercuric sulphite is not stable enough to enable it to be isolated except in combination with other sulphite, or with mercuric oxide or chloride. O. Ruff and E. Kröhnert found that the precipitate from mercuric chloride and an excess of ammonia dissolves when sulphur dioxide is passed through the liquid, and crystalline compounds of mercuric oxide with ammonia and sulphur dioxide are formed—*e.g.* **ammonium mercuric sulphite,** $Hg(NH_4SO_3)_2$—when the soln. is evaporated under reduced press. The reaction is symbolized: $HgCl_2+2H(HSO_3)+4NH_3=Hg(NH_4SO_3)_2+2NH_4Cl$. If sulphur dioxide is first added, and then ammonia, an insoluble compound containing sulphur dioxide and ammonia is slowly deposited. The reaction is symbolized: $NH_2.Hg.Cl+H(HSO_3)=Cl.Hg(NH_4SO_3)$, in acid soln. The ammonium mercuric sulphite, with an excess of ammonia, forms a mixture of **ammonium mercuric hydroxysulphite,** $HO.Hg(NH_4SO_3)$, and white needles of **mercuric amminosulphite,** $HgSO_3(NH_3)$, or



$$Hg{<}\substack{SO_2\\NH_3}{>}O$$

by the reaction: $Hg(NH_4SO_3)_2+NH_3=HgSO_3NH_3+(NH_4)_2SO_3$. If a large amount of ammonium chloride is present, **ammonium mercuric chlorosulphite,** $NH_3Cl.Hg(HSO_3)$, is formed: $Hg(NH_4SO_3)_2+NH_4Cl+NH_3=NH_3Cl.Hg(NH_4SO_3)+(NH_4)_2SO_3$. The compound forms long white transparent needles, and is converted by 2*N*-KOH into yellow **mercuric amminoxysulphite,** $Hg_2O.SO_3(NH_3)$, or



$$O{<}\substack{Hg.\,SO_2\\Hg.NH_3}{>}O$$

A conc. soln. of ammonium hydroxide forms a soln. which appears to contain **mercuric tetramminosulphite,** $Hg(NH_3)_4SO_3$; and liquid ammonia yields this compound as a white powder along with ammonium sulphite. O. Ruff and E. Kröhnert add that in acidic soln. the sulphur, which receives a negative charge from oxygen, and in alkaline soln., the nitrogen, which receives a negative charge from hydrogen, possess a strong tendency to complex formation, and in ammoniacal soln., complexes corresponding to mercurammonium sulphites are formed.

According to W. Wicke, when mercuric chloride is treated with a sat. soln. of sodium hydrosulphite, **mercuric hydrosulphite,** $Hg(HSO_3)_2$, separates as a heavy, crystalline powder. E. Divers and T. Shimidzu obtained sodium mercuric sulphite in this way; but they prepared an aq. soln. of mercuric hydrosulphite, $Hg(HSO_3)_2$, which reacts as if it were a soln. of mercuric sulphite in sulphurous acid. Mercuric oxide can be dissolved in sulphurous acid without forming the precipitates observed by C. F. Rammelsberg, L. P. de St. Giles, and A. Vogel. The sulphurous acid must not contain much sulphuric acid—from atm. oxidation—and the mercuric oxide must be prepared by precipitation, must be added well divided and suspended in water to the sulphurous acid, and only in small quantity, because only a weak soln. can be prepared. A soln., the same in every respect, can be obtained by using mercuric oxysulphite in place of mercuric oxide. Mercurosic sulphite, and hypomercurosic sulphite can also be used in place of the oxide, but then there is a residue of metallic mercury. An impure soln. can be prepared by cautiously adding, in small quantity, a soln. of either mercuric nitrate or sulphate, or of mercurous nitrate or solid mercurous sulphate or mercuric oxysulphate to sulphurous acid; with mercurous salts, half the mercury separates in an insoluble form, and with all these salts either sulphuric or nitric acid remains in the soln. Even by the action of a little nitric acid on sodium mercuric sulphite a dil. mercuric hydrosulphite soln. can be obtained; while a nearly boiling soln. of mercuric chloride is converted by a current of sulphur dioxide into mercurous chloride, hydrochloric acid, and sulphuric acid; but not so with a cold soln. E. Divers and T. Shimidzu found mercuric chloride to be more soluble in sulphurous acid than in water; if sulphuric acid be present, mercuric chloride is no longer so soluble in sulphurous acid. Sulphurous acid sat. with mercuric chloride will dissolve more mercuric oxide than it would do otherwise. It is assumed that the soln. of mercuric chloride in sulphurous acid forms a soln. of the hydrosulphite: $HgCl_2+2H_2SO_3=Hg(HSO_3)_2+2HCl$, and by dissolving mercuric oxide, it becomes saturated with mercuric hydrosulphate. Mercuric chloride is also more soluble in a soln. of sodium sulphite or pyrosulphite, forming sodium mercuric sulphate. Although A. Vogel said that sulphurous acid converts mercurous chloride into a grey subchloride, E. Divers and T. Shimidzu said that the action must be very slight because when mercurous chloride is precipitated by sulphurous acid, it is of dazzling whiteness. They attributed the grey discoloration to the presence of impurities, and added that it is doubtful if purified mercurous chloride will react with sulphurous acid.

A soln. of mercuric hydrosulphite is very unstable, and readily suffers hydrolysis, either wholly or in part—wholly into mercury and sulphuric acid, in part into mercurosic sulphite and sulphuric acid—sulphurous acid remaining free in both cases. The soln. deposits all its mercury slowly at common temp., but at once when heated, and an eq. quantity of sulphuric acid remains in soln.: $H_2O+Hg(SO_3H)_2=Hg+HO.SO_3H+H.SO_3H$. Partial hydrolysis, by which mercurosic sulphite is formed, is brought about in two ways. Sulphuric or nitric acid, added in small but sufficient quantity, causes it. Secondly, it is caused by adding more mercuric oxide or some mercuroxylic salt (best, a soln. of mercuric nitric or sulphate) to the soln. Whether the addition proves sufficient or not to exhaust all free sulphurous acid is a circumstance which does not affect the precipitation. Success with such different reagents renders it improbable that the hydrolysis depends on any direct reaction between them and the mercuric hydrogen sulphite. The change is induced by effecting a state of supersaturation of the soln. with mercuric hydrosulphite, so that partial hydrolysis occurs and mercurosic sulphite is precipitated. Mercury sulphites are insoluble in dil. nitric or sulphuric acid, and therefore the addition of one of these acids brings about the state of supersaturation, which leads to the sudden hydrolysis and precipitation. Mercuric oxide or salts generate more acid sulphite in the soln., and in this way cause supersaturation. Accordingly, mercuric hydrosulphite must be regarded as a salt soluble in a large quantity of water, and hydrolyzed by less water. The result of the hydrolysis of mercuric hydrogen sulphite when it has only proceeded to the extent of separating one-third of the sulphur as sulphuric acid, appears to depend on the difference between oxylic and non-oxylic mercury compounds; the mercuric radicle, Hg, alone can hold the non-oxylic position in a sulphite, the mercurous radicle, Hg_2, cannot. The mercurous radicle, on the other hand, can hold the oxylic position, provided a mercuric radicle is in non-oxylic relation to the sulphuryl, whilst the mercuric radicle cannot do so, except in the partial and complex way seen in the basic mercuric oxysulphite. Accordingly, the conversion of mercuric hydrogen sulphite to mercurosic sulphite may be represented by the following equation, in which the upper line shows the hydrolysis of a third of the sulphite, and the lower the double decomposition whereby, with the assistance of mercury set free by hydrolysis, two molecules of mercury hydrogen sulphite become mercury sulphite and hydrogen sulphite:

$$\left.\begin{array}{l}Hg''(SO_3H)_2+H_2O\\ Hg''(SO_3H)_2+Hg''(SO_3H)_2\end{array}\right\}=\left\{\begin{array}{l}H.SO_3H+HO.SO_3H\\ 2H.SO_3H+Hg''(SO_3)_2Hg'_2\end{array}\right.$$

The silver and mercury sulphites are not liable to atm. oxidation.

L. P. de St. Gilles prepared **mercuric oxysulphite,** $HgO.HgSO_3$, from a soln. of mercuric oxide in one of mercuric nitrate, by treatment with a dil. soln. of an alkali sulphite; and by mixing crystals of mercuric oxynitrate with a dil. soln. of an alkali sulphite—mercuric acetate gives no precipitate, and the oxalate and phosphate give double salts which are decomposed by boiling. E. Divers and T. Shimidzu prepared the oxysulphite from soln. of sodium sulphite or sodium mercuric sulphite and mercuric nitrate—or, if the soln. be strongly alkaline, with mercuric sulphate; and by the action of silver sulphite on a soln. of mercuric nitrate. They represented the constitution: $Hg(SO_2.O.Hg.O)_2Hg$, and found that when dried at ordinary temp. the salt is monohydrated, but becomes anhydrous in vacuo. Mercuric oxysulphite is a faint yellow, curdy or granular, dense salt, which is unstable, and changes to mercurous sulphate in a few hours. The salt is very explosive, but not violently so. Water causes mercuric oxysulphite to decompose more rapidly than it does when kept dry. Heated with water it decomposes, the change being at first probably the same as when it is heated dry; but the water effects a further change, and the products are mercurous sulphate, mercuric oxysulphate, sulphuric acid, and mercury. When dissolved in aq. sulphurous acid and boiled, it decomposes in the manner which seems normal to a non-basic mercury sulphite, the sole products being mercury and sulphuric acid. Potassium hydroxide converts it into insoluble mercuric oxide, and mercuric potassium sulphite in soln.: $Hg(SO_2OHgO)_2Hg+2KOH=Hg(SO_2OK)_2+3HgO+H_2O$. Hydrochloric acid, added in excess at once, converts it into mercuric chloride and sulphurous acid. Hydrochloric acid, gradually added, causes the change of part of it into mercurosic and even hypomercurosic sulphite, by the sulphurous acid liberated from another part; and hydrochloric acid then forms mercurous chloride. If it changes at all into mercurous sulphate, some mercurous chloride and sulphuric acid will also be produced, but sulphurous acid, even in the nascent state, will also be produced. If, again, it contains any of its mother-liquor of mercuric nitrate, reactions will take place on adding the hydrochloric acid, which will also produce mercurous chloride and sulphuric acid, the liberated sulphurous acid forming mercurosic sulphite from the nitrate, and the mercurosic sulphite forming mercurous chloride with the mercuric chloride. Nitric acid, or even sulphuric acid, if sufficiently dilute, hardly dissolves it, but hastens its change to mercurous sulphate. When a little more concentrated, the nitric or sulphuric acid dissolves it, without liberating sulphur dioxide, and then, if hydrochloric acid is added to the soln. without delay, mercuric chloride and sulphur dioxide are formed in considerable quantities, besides some mercurous chloride and sulphurous acid. But if the soln. is kept for a few minutes, mercurous sulphate takes the place of mercuric oxysulphite, and soon begins to separate. The addition of hydrochloric acid now produces only mercurous chloride and sulphuric acid. Sufficiently conc. sulphuric or nitric acid liberates sulphur dioxide at once from mercuric oxysulphite. Sulphurous acid, free or nearly free from sulphuric acid, when added in excess at once, dissolves it without forming any sulphate or sulphuric acid, and leaving mere traces of metallic mercury, the results of previous changes in the oxysulphite; when, however, the sulphurous acid is added gradually, mercurosic sulphite is formed, then hypomercurosic sulphite, and, lastly, metallic mercury, as the quantity of sulphurous acid increases, while the soln. from the first contains sulphuric acid, and, for a time, a little (acid) mercuric sulphite. The precipitation of mercurosic sulphite is also quickly induced when the sulphurous acid is added at once, provided it contains a good quantity of sulphuric acid. The formation of the mercurosic sulphite is represented: $3(OHg_2SO_3)_2+5H_2SO_3=3H_2SO_4+4Hg_3(SO_3)_2+2H_2O$. Sodium sulphite soln., added quickly in excess, dissolves it as mercuric sodium sulphite; a minute quantity of metallic mercury is left, due to the presence of a little mercurous sulphate formed by a previous change of the oxysulphite. Sodium hydroxide is also formed; $(OHg_2SO_3)_2+6Na(SO_3Na)+2H_2O=4NaOH+4Hg(SO_3Na)_2$. When the sodium sulphite is added gradually, however, black, flocculent hypomercurosic sulphite is first seen, which is subsequently resolved into mercury and mercuric sodium sulphite. This production of hypomercurosic sulphite seems to prove that when only partially attacked by sodium sulphite, the mercuric oxysulphite is decomposed in such a way that the basic oxide is removed, and the normal sulphite left to suffer a change practically the same as hydrolysis, but effected by the sodium hydroxide which has been formed along with it, instead of by water. Thus: $2Hg(SO_2O)_2Hg_3O_2+8Na(SO_3Na)+4OH_2=2Hg(SO_2O)Hg+4Hg(SO_3Na)_2+8NaOH$; and $2Hg(SO_2O)_2Hg+4NaOH=Hg(SO_2O)_2Hg_3+2Na_2SO_4+2OH_2$. Silver sodium sulphite soln. dissolves mercuric oxysulphite, all the silver being precipitated, principally as sulphate. The precipitate is much discoloured, apparently by the presence of a little mercuric argentous sulphite (coming from mercurous sulphate). Silver oxide scarcely appears, because the original soln. always contains some free sodium sulphite, and accordingly sodium hydroxide is found in soln. instead. Sodium chloride soln. forms mercuric oxide, yellow and insoluble, and mercuric sodium sulphite and mercuric sodium chloride, both in soln.: $(OHg_2SO_3)_2+4NaCl=2HgO+Hg(SO_3Na)_2+HgCl_4Na_2$. A little mercurous chloride is found with the oxide, and a little sodium sulphate in the soln., owing to the mercuric oxysulphite having begun to change into mercurous sulphate by the time it is prepared for experiment. Potassium iodide soln. changes mercuric oxysulphite instantly into a dull red compound, soluble in excess of the reagent, but with much more difficulty than simple mercuric iodide, and then yielding an alkaline soln. This dull red substance is of complex nature, and consists of mercuric iodide, oxide, and sulphite, in some state of combination. Except when the soln. of potassium iodide is very concentrated, the dissolution of the red compound is at once followed by the appearance of a slight yellow precipitate convertible by a more conc. soln. of potassium iodide into a minute quantity of metallic mercury and dissolved mercuric iodide. The production of this yellow iodide is to be referred to the presence of some mercurous sulphate in the mercuric oxysulphite. Mercuric chloride soln. acts slowly on mercuric oxysulphite, if at all, mercurous chloride being gradually produced, together with mercuric sulphate which remains in soln. with the excess of mercuric chloride. By dissolving mercuric oxysulphite in sulphuric acid before adding the mercuric chloride, the precipitation of mercurous chloride begins immediately, and proceeds rapidly until all the sulphite has been decomposed. Actually, mercuric chloride has probably no action on mercuric oxysulphite, its action being on the mercurous sulphate into which the oxysulphite so readily changes. The action of mercuric chloride on other mercury sulphites is sharp and unmistakable, and in their case the completion of the action is retarded, instead of advanced, by the presence of sulphuric acid. Mercuric iodide, oxide, nitrate, and sulphate, and also mercurous nitrate and sulphate, are without action. Silver nitrate also is without action on the oxysulphite itself, but a little silver is taken up apparently through the reaction with the mercurous sulphate present. L. P. de St. Gilles said that the oxysulphite is soluble in a soln. of potassium cyanide.

C. H. Hirzel prepared **ammonium mercuric sulphite,** $(NH_4)_2Hg(SO_3)_2$, or, according to E. C. Franklin, $(2HgO.HgSO_3)(NH_2Hg)_2SO_3$. C. H. Hirzel obtained it by dissolving freshly precipitated mercuric oxide in boiling sulphurous acid and saturating the soln. with conc. ammonia; K. Barth obtained it from a soln. of mercuric oxide in a hot, conc. soln. of ammonium sulphite. The salt furnishes transparent, colourless, doubly refracting plates; and K. Barth found that the dry salt rapidly decomposes into mercury, sulphur dioxide, and ammonium sulphate. According to C. H. Hirzel, the salt is sparingly soluble in water, and the cold, aq. soln. slowly decomposes into mercury and sulphuric acid with the evolution of sulphuric acid; the soln. can be boiled without decomposition if free ammonia be present. Sulphuric acid gives a white precipitate and drives off the sulphur dioxide; nitric acid in the cold gives a white precipitate which dissolves when the mixture is warmed and red fumes are given off; and potash-lye displaces ammonia and gives a white precipitate of *mercuric oxymercuriammonium sulphite*, $HgSO_3[NH_2(HgOHg)]_2SO_3$. With a hot soln., auric chloride forms gold-amalgam; a little hydrochloroplatinic acid gives a brown precipitate, and excess, a black precipitate; a little silver nitrate in the cold gives a white precipitate, and when boiled, the precipitate becomes yellow, brown, and black, sulphur dioxide is given off, and a silver amalgam is formed; lead nitrate gives a white precipitate in the cold, and when heated the precipitate blackens and lead amalgam is formed; and in the cold cupric sulphate gives no precipitate, but when boiled, copper-amalgam is formed. K. Barth prepared **ammonium mercuric chlorosulphite,** $(NH_4)_2Hg(SO_3)_2.HgCl_2$, or $NH_4ClHgSO_3$, by a method similar to that employed for the potassium salt—*vide infra.* The same remarks apply to **ammonium mercuric bromosulphite,** $(NH_4)_2Hg(SO_3)_2.HgBr_2$, or $NH_4BrHgSO_3$.

As indicated above, mercuric oxide reacts with a soln. of sodium sulphite, and F. Teltscher found that with a soln. of mercuric nitrate and sodium chloride, a white precipitate is formed when the molar proportion is 1 : 2—the precipitate immediately blackens. If the proportion is 1 : 4 no precipitation occurs, but the soln. becomes turbid. F. Teltscher studied the potential and light sensitiveness of these soln. K. Barth obtained a basic salt, **sodium mercuric oxydisulphite,** $Na_2O.2HgSO_3$, or $O(HgSO_3Na)_2$. It is best made by mixing hot conc. soln. of mercuric chloride and sodium sulphite in molar proportions with the corresponding quantity of sodium hydroxide; adding alcohol; and cooling the soln. The needle-like crystals lower the f.p. of water, giving a mol. wt. of 180–190 when the calculated value is 622. The eq. conductivity, λ, for an eq. of the salt in v litres is:

v . . .	16	32	64	128	256	512	1024
λ . . .	65·4	69·3	73·0	75·7	77·5	78·6	79·3

When treated with oxy-acids, a grey precipitate of *mercury oxytetrasulphite*, $O(HgSO_3.HgSO_3.Hg)_2Hg$, is formed. L. P. de St. Gilles reported **sodium mercuric trisulphite,** $Na_2SO_3.2HgSO_3.H_2O$, to be formed in needle-like crystals, by mixing a hot, sat. soln. of sodium sulphite and an excess of mercuric chloride, and cooling the filtered soln. E. Divers and T. Shimidzu, and K. Barth could not prepare this salt. L. P. de St. Gilles prepared sodium mercuric sulphite, $Na_2SO_3.HgSO_3.H_2O$, which E. Divers and T. Shimidzu represented by $Hg(SO_2.ONa)_2.H_2O$. L. P. de St. Gilles made it by pouring a soln. of mercuric chloride into an excess of one of sodium sulphite, and evaporating—H. Baubigny, and K. Seubert and M. Elten employed an analogous process. K. Barth obtained it from a soln. of mercuric oxide in one of sodium hydrosulphite; and E. Divers and T. Shimidzu, from a soln. of mercuric oxide in one of sodium pyrosulphite—if normal sodium sulphite be used, some sodium hydroxide is formed. When sodium sulphite acts on mercurous chloride, hypomercurosic sulphite is precipitated, but this is so rapidly decomposed by the excess of sodium sulphite, forming sodium mercuric sulphite and mercury, that it is only just possible to see the blackening of the sulphite. The end-products are: $2HgCl+2Na_2SO_3=Na_2Hg(SO_3)_2+Hg+2NaCl$. The reaction is quantitative—half the mercury passes into soln., and half is precipitated as black mercury. The colourless crystals are comparatively stable. When the dry salt is moderately heated, it evolves sulphur dioxide and water, and becomes brown or grey. When the residue is wetted, it blackens, through the formation of a flocculent, brownish-black matter, in small quantity, the principal products being metallic mercury and sodium sulphate. The brown-black matter heated with water changes into a pure black substance, insoluble in hot dil. nitric acid, and which is apparently mercuric sulphide. The main change effected by dry heat is probably the same as that by hot water, but a little mercuric sodium thiosulphate would seem to be also produced, by a reaction between the sulphur dioxide and some as yet undecomposed mercuric sodium sulphite. K. Barth found the lowering of the f.p. of aq. soln. corresponds with a mol. wt. of 153·6–154·9—theory requires 406·6. The eq. conductivity, λ, for an eq. of the salt in v litres is:

v . .	16	32	64	128	256	512	1024
λ . .	79·4	85·8	91·0	95·4	98·7	102·8	106·5

L. P. de St. Gilles found that the aq. soln. is sparingly soluble in water and neutral to litmus; and, added E. Divers and T. Shimidzu, 100 parts of cold water dissolve about 4 parts of the salt. The aq. soln. may be preserved a little time without change, but it slowly turns grey, and decomposes into sulphur dioxide, mercury, and sodium sulphate. H. Baubigny, and K. Barth made observations to the same effect. According to L. P. de St. Gilles, when the aq. soln. is heated, similar products are obtained: $Hg(SO_3Na)_2=Hg+SO_2+Na_2SO_4$, and the change is abrupt. He said that mercurous sulphate is one of the first products of the decomposition by hot water: $2Hg(SO_3Na)_2=Hg_2SO_4+Na_2SO_3+Na_2S_2O_5$, and the mercurous sulphate blackens rapidly and dissolves leaving only mercury as a residue. H. Baubigny observed that no dithionate is formed. E. Divers and T. Shimidzu said that it is not likely that mercurous sulphate is formed, for it would not come out of a soln. with an abundance of hot acid liquor, and it cannot exist in the presence of sodium sulphite. The separation attributed to mercurous sulphate is produced by the separation of mercury which first appears as a bright rolling cloud, suggesting a precipitate of great volume, an effect due apparently to metallic reflection of light; this cloud then melts away, leaving a relatively minute, very dark grey deposit of mercury at the bottom of the vessel, the bright mist becomes, so to speak, a rain of mercury. The effect of sodium hydroxide, sulphite, and chloride in preventing the decomposition of the salt in hot soln. indicates that the decomposition which occurs in absence of all such substances depends on the presence of acid, develops in minute quantity by the incipient decomposition of the salt. As to the sodium chloride, that will be effective through its displacing the sulphuric acid from the sulphite by hydrochloric acid, which is incapable of causing any liberation of mercury from the double sulphite. Since acid is the cause of the change, the formation of mercurosic sulphite will precede that of free mercury. Sodium hydroxide is without action when in dil. soln. (L. P. de St. Gilles); in its presence a soln. of mercuric sodium sulphite can be boiled without decomposing. If, however, the sodium hydroxide is added in somewhat large quantity and in conc. soln., it precipitates some of the mercuric oxide, slowly in the cold, rapidly in the hot soln. Some only of the oxide is precipitated, and this is the scarlet-red form, instead of the usual orange-yellow one. In thus yielding the red oxide, mercuric sodium sulphite resembles black mercuric oxychloride. Potassium hydroxide precipitates mercuric potassium sulphite, which is much less soluble than the sodium salt. Mercuric oxide is not precipitated from the potassium salt by the most conc. soln. of potassium hydroxide, even when hot. Hydrochloric acid changes it into mercuric sodium chloride and sulphurous acid. Nitric acid (or sulphuric acid) sufficiently diluted, and not in great excess, yields mercurosic sulphite, sodium sulphate and nitrate, and sulphur dioxide; thus: $3Hg(SO_3Na)_2+4HNO_3=4NaNO_3+Na_2SO_4+Hg_3(SO_3)_2+3SO_2+2H_2O$. In this complex change, the mercuric sulphite will not be decomposed by the nitric acid itself, for dil. nitric acid does not decompose mercury sulphites. The double salt will first exchange its sodium for the hydrogen of the nitric acid, and then the mercuric hydrogen sulphite will suffer partial hydrolysis and be converted into mercurosic sulphite, sulphuric acid, and sulphurous acid. The addition of a little acid to a soln. of mercuric sodium sulphite makes it smell of sulphur dioxide, but does not cause immediate precipitation. Some greyish mercurosic sulphite may soon precipitate, but in any case mercury is gradually set free. The acidified soln. behaves, in fact, as one of mercuric hydrosulphite. Sulphurous acid is without an apparent action. Sodium sulphite, in dil. soln., is without action, but its presence stops the decomposition of mercuric sodium sulphite by heat; in conc. soln., it precipitates much of the mercuric sodium sulphite, which is much less soluble in it than in water, slightly soluble only as it is in the latter. Sodium chloride soln. is without action; it prevents (L. P. de St. Gilles), or almost prevents, the usual decomposition when mercuric sodium sulphite is heated alone with water. The evaporated soln. deposits crystals of the mercuric sodium sulphite unchanged, according to L. P. de St. Gilles. Sodium hydroxide has no effect on the boiling mixed soln., indicating that there is no action (L. P. de St. Gilles) when the sulphite is in soln. A soln. of the iodide added to the solid sulphite gives a little crimson (not yellow or scarlet) precipitate. The mother-liquor, or a mixed soln. of the sulphite and iodide, gives a precipitate of ordinary mercuric iodide when treated with sulphur dioxide. Mercuric chloride soln., in the cold, is without action; but when the soln. are hot, mercurous chloride, sodium sulphate, and sulphur dioxide are produced: $Cl_2Hg+Hg(SO_3Na)_2=(ClHg)_2+SO_4Na_2+SO_2$. Or, as L. P. de St. Gilles found, hydrochloric acid may be formed (and then there will also be sulphuric acid): $2H_2O+3Cl_2Hg+Hg(SO_3Na)_2=2HCl+2(ClHg)_2+SO_4Na_2+SO_4H_2$. This occurs only when the mercuric chloride is in excess, the two acids then resulting from the well-known reaction between mercuric chloride and sulphurous acid. It is almost certain that the formation of mercurous chloride is due to the independent decomposition of the mercuric sodium sulphite, for when this is prevented by the addition of sodium chloride no change of mercuric chloride to mercurous chloride takes place. Mercurosic sulphite is formed from the mercuric sodium sulphite by the action of traces of sulphuric acid, and the mercuric chloride then acts on it, to yield mercurous chloride and sulphuric acid again; so that once started, the decomposition of the sulphite proceeds very quickly. Mercuric iodide is without action in the cold. Heated, it is converted into the yellow iodide, and ultimately to mercurous iodide apparently. The reaction will be similar to that between the sulphite and mercuric chloride. Mercuric oxide (precipitated) is without action in the cold, but warmed with the soln. it gradually gives places to somewhat grey mercurosic sulphite, sodium sulphate being also formed. Most probably some decomposition of the mercuric sodium sulphite first occurs, as usual, into sodium sulphate, mercurosic sulphite (or mercury), and sulphurous acid, and then the sulphurous acid reacts with the mercuric oxide to form more mercurosic sulphite and sulphuric acid, which with sodium sulphite gives sodium sulphate and sulphurous acid, and so on. Mercuric nitrate soln. (aq. nitric acid sat. with precipitated mercuric oxide), in excess, dissolves mercuric sodium sulphite, and then very rapidly yields a precipitate of mercuric oxysulphite. Provided the mercuric nitrate soln. is somewhat conc. (10 per cent. or more), and free from avoidable excess of acid, oxysulphite alone is precipitated if the mercuric sodium sulphite is added at once in quantity small enough to leave much of the nitrate undecomposed, and consequently not to generate too much nitric acid in this soln. The formation of the oxysulphite appears to be the only reaction of the mercuric nitrate itself, but other changes occur, owing to the nitric acid set at liberty: $3Hg(NO_3)_2+Hg(SO_3Na)_2+2H_2O=2NaNO_3+4HNO_3+(OHg_2SO_3)_2$. The mother-liquor of the oxysulphite, treated with more mercuric sodium sulphite, yields at first mercurosic sulphite, and then gradually mercurous sulphate. When the quantity of the sulphite first added to the mercuric nitrate is too great, mercurosic sulphite may or may not be precipitated, but the oxysulphite which is formed remains in soln., soon, however, to pass, with marked rise of temp., into mercurous sulphate, which then crystallizes out. In this case, it is sometimes quite practicable to pour the mother-liquor off from the mercurosic sulphite, before the mercurous sulphate begins to separate. Mercurosic sulphite can always be obtained by adding the mercuric nitrate gradually to the mercuric sodium sulphite. It is no doubt formed, in either case, through the action of the nitric acid present on the mercuric sodium sulphite, and of liberated sulphurous acid on the mercuric nitrate; whilst the mercurous sulphate is the result of a metameric change of the mercuric oxysulphite in soln. in the nitric acid. Mercurous nitrate soln. precipitates mercurosic sulphite: $Hg(SO_3Na)_2+(HgNO_3)_2=2NaNO_3+Hg(SO_3)_2Hg_2$. Mercurosic sulphite prepared in this way is always of a light buff colour, although when formed by hydrolysis it is brilliantly white. When the nitrate soln. is free from nitrous acid, and, so far as possible, from nitric acid also, only traces of sulphuric acid are formed. Nitric acid, in precipitating mercurosic sulphite, generates sulphuric acid. Mercuric sulphate soln. does not precipitate mercuric oxysulphite, in consequence, apparently, of the solubility of the latter in sulphuric acid. The mixed soln. soon deposits mercurous sulphate. By adding quickly about an eq. quantity of the mercuric sodium sulphite, mercurosic sulphite can be precipitated. By adding a little strongly alkaline soln. of mercuric sodium sulphite to excess of conc. mercuric sulphate soln., mercuric oxysulphite can be precipitated. Mercurous sulphate behaves like the nitrate, when it is shaken in the solid state with soln. of mercuric sodium sulphite. It is then quickly changed to mercurosic sulphite. K. Barth prepared **sodium mercuric chlorosulphite,** $HgCl_2.Na_2Hg(SO_3)_2.H_2O$, or $NaClHgSO_3.H_2O$, by a method analogous to that used for the potassium salt—*vide infra.*

K. Barth prepared **potassium mercuric oxytrisulphite,** $K_2O.3HgO.3SO_2$, or $KSO_3.Hg.O.Hg.SO_3.Hg.SO_3K$, by shaking a soln. of potassium mercuric chlorosulphite with an excess of moist silver oxide, or with potassium hydroxide, and evaporating the soln. on a water-bath; or else by mixing one part of mercuric oxide with 2 parts of a soln. of potassium hydrosulphite. The dry salt quickly decomposes; it is insoluble in water; partially soluble in potash-lye; and develops sulphur dioxide without oxidation when treated with the halogen acids. K. Barth also prepared **potassium mercuric oxydisulphite,** $K_2O.2HgO.2SO_2$, or $O(HgSO_3K)_2$; and *monohydrate*, $K_2O.2HgO.2SO_2.H_2O$, or $HO.HgSO_3K$, in groups of needle-like crystals, by adding alcohol to the liquor obtained by treating the preceding salt with alcohol. It decomposes suddenly with detonation at 91°. E. Divers and T. Shimidzu obtained **potassium mercuric sulphite,** $K_2SO_3.HgSO_3.nH_2O$, as a precipitate by adding potash-lye to a soln. of the sodium salt. L. P. de St. Gilles obtained the *monohydrate* from sat. soln. of mercuric chloride and potassium sulphite; from a soln. of mercuric oxide or mercuric iodide in one of potassium sulphite; and from the soln. obtained by treating mercurous chloride with potassium sulphite soln. K. Barth reported that the salt is a *dihydrate*, $K_2SO_3.HgSO_3.2H_2O$. The white needles of the monohydrate give off water when heated; and at a higher temp., most of the mercury is volatilized and potassium sulphate remains. K. Barth found that the lowering of the f.p. corresponds with a mol. wt. of 168·2 to 171·8—theory 438·8. The eq. electrical conductivity, λ, for an eq. of the salt in v litres is:

v . .	16	32	64	128	256	512	1024
λ . .	97·3	104·0	110·2	115·5	119·5	123·1	126·0

The results correspond with the ionization of the salt into three ions. The salt is sparingly soluble in cold water, forming a neutral soln.; when the aq. soln. is heated, it decomposes: $2(K_2SO_3.HgSO_3)+H_2O=Hg_2SO_4+K_2SO_3+2KHSO_4=2Hg+2K_2SO_4+2SO_2+H_2O$—*vide supra,* the corresponding sodium salt. Hydrochloric acid, in a boiling soln., gives a quantitative yield of sulphur dioxide without reduction. In a boiling soln. mercuric chloride is reduced: $K_2SO_3.HgSO_3+HgCl_2=2HgCl+K_2SO_4+SO_2$. No precipitate is formed with potassium hydroxide, iodide, ferrocyanide, ferricyanide, or with alkali phosphate, carbonate, oxalate, or tartrate. Hydrogen sulphide, or alkali hydrosulphide, gives an orange-yellow, or a black precipitate. K. Barth also prepared **potassium mercuric chlorosulphite,** $K_2Hg(SO_4)_2.HgCl_2$, from a hot sat. soln. of the component salts. The lowering of the f.p. of water corresponds with a mol. wt. of 176·5—theory 710. The crystal plates and needles are easily decomposed especially in boiling aq. soln. Oxy-acids accelerate the decomposition of the salt; halide acids give sulphur dioxide and mercuric halide; metal chlorides and alkali sulphites do not decompose the salt. Alkali phosphate, carbonate, oxalate, and tartrate give no precipitation; potassium ferrocyanide and ferricyanide give precipitates; and with alkali hydroxides, the chlorine is replaced by oxygen or the hydroxyl-radicle. The corresponding **potassium mercuric bromosulphite,** $HgBr_2.K_2Hg(SO_3)_2$, was obtained in a similar way, and its properties were the same.

E. Divers and T. Shimidzu found that a **silver mercuric sulphite,** $Ag_2SO_3.HgSO_3.2H_2O$, is probably formed on adding sodium silver sulphite to hypomercurosic sulphite. The formula here given is due to K. Barth, who prepared this salt by adding silver nitrate to alkali mercuric sulphite. The white precipitate decomposes in a few minutes, becomes brown and black from the separation of mercury and silver. **Cupric mercuric sulphite,** $CuSO_3.HgSO_3$, is freely soluble in water, and the soln. is decomposed when boiled. By adding a soln. of a strontium salt to the alkali mercuric sulphite he obtained a crystalline precipitate of **strontium mercuric sulphite,** $SrSO_3.HgSO_3.2H_2O$; similarly with **barium mercuric sulphite,** $BaSO_3.HgSO_3.H_2O$.

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§ 20. The Sulphites of the Aluminium-Rare Earth Family

A. F. de Fourcroy and L. N. Vauquelin[1] prepared **aluminium tetrahydroxysulphite,** $Al(OH)_3.Al(OH)SO_3$, or $Al_2(OH)_4SO_3$, from a soln. of aluminium hydroxide in sulphurous acid. M. Gougginsperg evaporated the soln. in vacuo, and obtained a gummy mass, but by heating the soln. to 74°, this salt is precipitated as a white powder. Analyses by A. H. Röhrig, J. S. Muspratt, A. F. de Fourcroy and L. N. Vauquelin, and M. Gougginsperg agree with this formula. The salt gives off sulphur dioxide at 100°, and when heated to a higher temp., alumina contaminated with a little sulphate is formed. The salt is insoluble in water ; soluble in sulphurous acid ; and it oxidizes in air to a basic sulphate. K. Seubert and M. Elten mixed 0·1*N*-soln. of 2 mols of aluminium chloride and 3 mols of sodium sulphite, cold or hot—sulphur dioxide is at the same time evolved—and a white gelatinous precipitate is formed. This was washed with cold or hot water and dried in vacuo. Its composition corresponded with **aluminium octohydroxytrisulphite,** $6Al(OH)_3.Al_2(SO_3)_3.9H_2O$. The salt is readily oxidized in air. G. Scurati-Manzoni made a mixture of powdered aluminium sulphate and sodium sulphite, and heated it with a little water to 100°. On cooling, sodium sulphate crystallized out, and what may have been normal **aluminium sulphite** remained in soln.

According to L. E. Porter and P. E. Browning, if neutral or acidic soln. of a *gallium salt* be treated with an ammoniacal soln. of ammonium hydrosulphite and boiled, gallium hydroxide is precipitated under conditions where a soln. of the zinc salt would not be precipitated. According to C. J. Bayer, if indium hydroxide be treated with an excess of a soln. of sodium hydrosulphite, or, according to A. Thiel, with ammonium sulphite, and boiled, a white crystalline precipitate of **indium oxysulphite,** $In_2O_3.In_2(SO_3)_3.8H_2O$, is formed. It loses 3 mols. of water at 100° ; at 280° the evolution of sulphur dioxide begins ; and at a red-heat indium oxide is formed.

If sulphur dioxide be passed into a soln. of thallous salt, the turbidity first formed soon vanishes, and on evaporating the soln. in a desiccator, or on a water-bath, scaly crystals of **thallous sulphite,** Tl_2SO_3, are produced ; K. Seubert and M. Elten obtained the same salt from a mixture of soln. of molar proportions of thallous sulphate and sodium sulphite. The precipitate was allowed to stand in contact with its mother liquid for 24 hrs., and then washed with 50 per cent. alcohol, and then with stronger alcohol. Alcohol precipitates the salt from its acid soln. The crystals are pale yellow. The sp. gr. is 6·4164 at 19·8°/0°. R. Robl observed no fluorescence with thallous sulphite in ultra-violet light. K. Seubert and M. Elten observed that the salt is fairly stable in air, but oxidizes slowly ; the crystals are sparingly soluble in cold, but freely soluble in hot water ; at 15°, 100 parts of water dissolve 3·34 parts of the salt. When treated with dil. acids, sulphur dioxide is given off, and when heated in hydrogen, thallous sulphide and sulphate, and thallium are formed. Boiling water forms a basic salt with the evolution of sulphur dioxide. **Thallous hydrosulphite,** $TlHSO_3$, has not been reported. G. Canneri prepared yellow crystals of **thallous cupric sulphite,** $Tl_2Cu(SO_3)_2$, and blue crystals of the *hexahydrate*, $Tl_2Cu(SO_3)_2.6H_2O$; as well as cinnabar red crystals of **thallous cuprosic sulphite,** $CuSO_3.3Cu_2SO_3.Tl_2SO_3$. He also made **thallous zinc sulphite,** $Tl_2Zn(SO_3)_2$, and **thallous cadmium sulphite,** $Tl_2Cd(SO_3)_2$, as pink microcrystalline powders.

W. Crookes obtained a heavy white precipitate of **scandium sulphite,** $Sc_2(SO_3)_3$, by mixing soln. of scandium chloride and sodium sulphite, and drying in air. The salt is soluble in an excess of a hot sodium sulphite soln. It is insoluble in cold water and slightly soluble in hot water. R. J. Meyer obtained the *hexahydrate.* The salt is decomposed when boiled with water and sulphur dioxide is evolved. R. J. Meyer prepared **ammonium scandium sulphite,** $(NH_4)_2SO_3.Sc_2(SO_3)_3.7H_2O$, from its component salts ; it is insoluble in water, and sparingly soluble in sulphurous acid.

P. Berthier obtained needle-like crystals of **cerium sulphite,** $Ce_2(SO_3)_3.3H_2O$, from a soln. of cerous carbonate in sulphurous acid. The crystals are readily soluble in water. The soln. gradually decomposes. H. Grossmann said that cerium, lanthanum, and didymium sulphites exhibit no tendency to form complex sulphites with the alkali sulphites. V. Cuttica prepared **potassium cerous sulphite.** $K_2SO_3.Ce_2(SO_3)_3.4H_2O$, by adding an excess of the alkali sulphite to a soln. of the hydrosulphite of the rare earth, and subsequently heating the liquid, on a water-bath, in a flask connected with a water-pump, so that air is largely excluded, the double sulphite separates as a microscopic powder, which is highly stable in the air, but undergoes gradual oxidation to sulphate if suspended in water. Similarly, **ammonium cerous sulphite,** $3(NH_4)_2SO_3.2Ce_2(SO_3)_3$; and also normal **sodium cerous sulphite,** $Na_2SO_3.Ce_2(SO_3)_3.2H_2O$, and if a deficiency of sodium sulphite is present, $2Na_2SO_3.3Ce_2(SO_3)_2.2H_2O$ is formed. P. T. Cleve obtained a voluminous mass of **lanthanum sulphite,** $La_2(SO_3)_2.4H_2O$, from a soln. of the hydroxide in sulphurous acid ; V. Cuttica prepared **potassium lanthanum sulphite,** $3K_2SO_3.2La_2(SO_3)_3.2H_2O$, and **ammonium lanthanum sulphite,** $(NH_4)_2SO_3.La_2(SO_3)_3$. J. C. G. de Marignac obtained **didymium sulphite,** $Di_2(SO_3)_3.3H_2O$, or $6H_2O$, in a similar way. The salt is insoluble in water, and soluble in sulphurous acid, from which soln. it is precipitated by heating, and redissolves on cooling. V. Cuttica prepared **potassium didymium sulphite,** $K_2SO_3.Di_2(SO_3).4H_2O$. P. T. Cleve made **samarium sulphite,** $Sm_2(SO_3)_3.3H_2O$, as a white powder, by dissolving the oxide in sulphurous acid. The salt loses a mol. of water at 100°. P. T. Cleve obtained in a similar manner **erbium sulphite,** $Er_2(SO_3)_3.3H_2O$; **yttrium sulphite,** $Y_2(SO_3)_3.3H_2O$, which is slightly soluble in water ; and A. Cleve **ytterbium sulphite,** $Yb_2(SO_3)_3.9H_2O$, by the action of sulphur dioxide on water with the carbonate in suspension. It is insoluble in water. P. B. Sarkar prepared the *dodecahydrate* of **gadolinium sulphite,** $Gd_2(SO_3)_3.12H_2O$, by double decomposition of gadolinium nitrate with sodium sulphite ; and the *hexahydrate* by the action of sulphur dioxide on gadolinia suspended in water. G. Canneri and L. Fernandes prepared some cuprosulphites of the rare earths, with the general formula $RCu(SO_3)_2.8H_2O$, and in the form of minute crystals, by crystallizing under reduced press. a warm soln. of copper carbonate and the rare-earth hydroxide, sat. with sulphur dioxide. These compounds are darker in colour and much less stable than the corresponding compounds of the alkali metal. Thus, **cerium cuprous disulphite,** $CeCu(SO_3)_2.8H_2O$; **lanthanum cuprous disulphite,** $LaCu(SO_3)_2.8H_2O$; **praseodymium cuprous disulphite,** $PrCu(SO_3)_2.8H_2O$; and **neodymium cuprous disulphite,** $NdCu(SO_3)_2.8H_2O$, are known.

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§ 21. Sulphites of the Zirconium-Lead Family

R. Hermann [1] observed that ammonium sulphite precipitates a basic **zirconium oxysulphite** which dissolves in an excess of the precipitant. The soln. gives no precipitate with alkalies, and when boiled deposits zirconium hydroxide. F. P. Venable and C. Baskerville passed sulphur dioxide into a feebly ammoniacal soln. of zirconium chloride and obtained basic sulphites ; also by the action of sulphurous acid on zirconium hydroxide ; by the action of sodium sulphite on a feebly acidic soln. of zirconium chloride ; and C. Baskerville, by the action of sulphur dioxide on a feebly acidic soln. of zirconium chloride—not sulphate. The composition of these products was found by F. P. Venable and C. Baskerville to vary from the molar proportion Zr : SO_2=2 : 1 to 4 : 1. P. Berthier described the basic sulphite as a white powder, easily soluble in sulphurous acid, and precipitated by boiling the soln. F. P. Venable and C. Baskerville obtained crystals of normal **zirconium sulphite,** $Zr(SO_3)_2.7H_2O$, from a soln. of zirconium hydroxide in an excess of sulphurous acid, and evaporating the filtered soln. over conc. sulphuric acid.

C. Baskerville obtained a basic thorium sulphite of indefinite composition by passing sulphur dioxide into a soln. of thorium hydroxide in hydrochloric acid and neutralizing with ammonia ; and H. Grossmann observed the precipitation from thorium salt soln. by ammonium sulphite is quantitative. The precipitate is soluble in sulphurous acid. H. Grossmann obtained **thorium dihydroxytrisulphite,** $Th_2(OH)_2(SO_3)_3.37H_2O$, as a white precipitate by passing sulphur dioxide into a conc. soln. of thorium nitrate. P. T. Cleve obtained normal **thorium sulphite,** $Th(SO_3)_2.H_2O$, by deposition from a soln. of thorium hydroxide in sulphurous acid, and drying the white amorphous powder at 100°. A soln. of thorium sulphite gives a precipitate when treated with alkali hydrosulphite, and the precipitate—possibly *thorium hydrosulphite*—is only slightly soluble in an excess of the precipitant. No complex salt is formed when the hydroxide is dissolved in a soln. of alkali hydrosulphite. H. Grossmann obtained **potassium thorium hydroxysulphite,** $2K_2SO_3.Th(OH)_2SO_3.10H_2O$, as a white amorphous powder ; and **sodium thorium hydroxysulphite,** $2Na_2SO_3.Th_2(OH)_2(SO_3)_3.22H_2O$, as an insoluble solid, which is soluble in dil. hydrochloric acid.

A. F. de Fourcroy and L. N. Vauquelin [2] found that tin dissolved in sulphurous acid produces tin sulphide and sulphite. J. J. Berzelius said that stannous sulphide and thiosulphate are the main products, but M. J. Fordos and A. Gélis showed that very little thiosulphate is formed. The main product is stannous sulphite. P. Berthier found that ammonium sulphite precipitates almost the whole of the tin, as **tin oxysulphite,** from a cold soln. of stannous chloride, and all is precipitated from a boiling soln. According to A. Röhrig, a grey basic sulphite is precipitated when stannous chloride is added to an excess of alkali sulphite soln. ; with more stannous chloride, the precipitate redissolves, and some stannous sulphide separates out. If freshly precipitated and well-washed stannous hydroxide is treated with sulphur dioxide, a yellow basic salt, $5SnO.2SO_2.20H_2O$, soluble in sulphurous acid is formed ; and when the soln. is warmed, $11SnO.2SO_2.20H_2O$ is precipitated. K. Seubert and M. Elten mixed dil. soln. of stannous chloride and sodium sulphite, and after washing the precipitate and drying it in vacuo, obtained a product with the composition $Sn(OH)_2.16SnSO_3$.

J. L. Gay Lussac, and T. Thomson obtained **lead sulphite,** $PbSO_3$, by treating a soln. of a lead salt with alkali sulphite; H. Pellet used sulphur dioxide. K. Seubert and M. Elten poured a soln. of 12·58 grms. of sodium sulphite in 100 c.c. of air-free water into one of 37·8 grms. of lead acetate in 100 c.c. of air-free water; washed the precipitate with water, and dried it in vacuo. M. Griffin and M. Little, and G. S. Jamieson showed that the precipitation with sulphurous acid, or with sodium or ammonium hydrosulphite, is quantitative. W. N. Iwanoff also showed that the reaction is sensitive to one part of lead in 20,000,000. L. Marino added lead dioxide to a conc. soln. of ammonium hydrosulphite cooled by ice: $PbO_2+SO_2=PbSO_3+O$. A. Röhrig passed sulphur dioxide into water with lead carbonate in suspension. A. G. Fell passed sulphur dioxide into a soln. of lead acetate. R. Warrington treated lead phosphate with sulphur dioxide; H. C. H. Carpenter, lead dithionate; S. C. Smith, lead chloride; and A. Guerot, lead sulphide. G. F. Rodwell observed that some sulphite is formed when lead sulphide is exposed to moist air; and A. and L. Lumière and A. Seyewetz, by the action of lead pentathionate on sodium thiosulphate. Lead sulphite is a white, tasteless, granular powder, which oxidizes in light to lead sulphate. When heated, it develops sulphur dioxide and leaves a residue of lead sulphide, sulphate, and oxide. J. L. Gay Lussac, and T. Thomson found the sulphite to be insoluble in water; and K. Seubert and M. Elten showed that when boiled with water, it forms a basic salt, but a definite basic sulphite could not be prepared. A. G. Fell, A. and L. Lumière and A. Seyewetz, and A. C. J. Charlier proposed to use the basic sulphite obtained by the action of steam on the normal sulphite, or from a paste of lead oxide and sulphur dioxide under press., as a substitute for white lead. A. H. Röhrig found the sulphite is sparingly soluble in sulphurous acid, but soluble in other acids. J. L. Gay Lussac, and T. Thomson found that with hydrochloric and sulphuric acids, sulphur dioxide is given off; and with nitric acid, the salt is oxidized to sulphate. L. Marino found that the sulphite is quantitatively oxidized by potassium permanganate soln.; and with dimethyl sulphate it forms lead methyl sulphonate, and he inferred that the structure is asymmetric.

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§ 22. Sulphites of the Antimony-Vanadium Family

J. J. Berzelius[1] obtained what he regarded as **antimony sulphite** by the action of sulphurous acid on antimony trioxide, and by passing sulphur dioxide into an aq. soln. of antimony trichloride; but A. H. Röhrig was unable to prepare antimony sulphite by either of these methods.

K. Seubert and M. Elten were unable to prepare **bismuth sulphite,** $Bi_2(SO_3)_3$, **bismuthyl sulphite,** $(BiO)SO_3$, or **bismuth hydroxysulphite,** $Bi(OH)(SO_3)$. The products were more complex, and may be mixtures of two or more of these components. J. S. Muspratt obtained a sulphite which was not closely investigated by passing sulphur dioxide into a soln. of bismuth nitrate. A. F. de Fourcroy and L. N. Vauquelin, and A. Röhrig, obtained bismuthyl dihydroxytrisulphite, $(BiO)_2SO_3.2(BiOH)SO_3.4H_2O$, by treating bismuth oxide with sulphurous acid, and washing the product with alcohol, and drying it over sulphuric acid. The white powder is stable in air, insoluble in water; and soluble in sulphurous acid. K. Seubert and M. Elten obtained **bismuthyl hydroxydecasulphite,** $9(BiO)_2SO_3.Bi(OH)SO_3.2H_2O$, as a white powder, by pouring a boiling hot soln. of a mol of bismuth nitrate and nitric acid to a hot soln. of 4 mols of sodium sulphite; the precipitate was washed free from nitric acid by hot water, and dried over sulphuric acid; **bismuthyl hydroxypentasulphite,** $4(BiO)_2SO_3.(BiOH)SO_3.5H_2O$, was prepared by using a mol of bismuth nitrate and 8 mols of sodium sulphite, at ordinary temp.; **bismuthyl trihydroxypentasulphite,** $2(BiO)_2SO_3.3(BiOH)SO_3.2H_2O$, using a mol of bismuth nitrate and 4 mols of sodium sulphite at ordinary temp.; **bismuthyl heptahydroxydecasulphite,** $3(BiO)_2SO_3.7(BiOH)SO_3.10H_2O$, using a mol of bismuth nitrate and 3 mols of sodium sulphite; and **bismuthyl trihydroxytetrasulphite,** $(BiO)_2SO_3.3(BiOH)SO_3.H_2O$, by allowing the precipitate with a mol of bismuth nitrate and 4 mols of sodium sulphite, at ordinary temp., to stand in contact with its mother-liquid for some time before washing.

G. Gain[2] prepared **vanadyl trisulphite,** $4VO_2.3SO_2.10H_2O$, by dissolving in air-free sulphurous acid the mixture of vanadium tri- and tetra-oxides obtained by calcining ammonium vanadate at a dull red-heat. The soln. furnishes silky, blue needles of the salt. When the aq. soln. is boiled, it decomposes, forming pale red crystals of hypovanadic acid. I. Koppel and E. C. Behrendt prepared **vanadyl sulphite,** $3VO_2.2SO_2.4\frac{1}{2}H_2O$, by boiling a mol of ammonium vanadate with a soln. of an eq. quantity of barium hydroxide until the ammonia is completely expelled, and reducing the suspended barium vanadate with sulphur dioxide: $Ba(VO_3)_2+SO_2=BaSO_4+2VO_2$. The evaporation of the filtered liquid in a current of sulphur dioxide gave a dark blue, microcrystalline powder, whose composition is probably $H_2O.3VO_2.2SO_2.3\frac{1}{2}H_2O$. Vanadyl sulphite forms two series of complex salts. The blue series has the empirical formula $R'_2O.2SO_2.3VO_2.nH_2O$; and the green series $R'_2O.2SO_2.VO_2.nH_2O$. The blue series is obtained by mixing a mol of ammonia with a soln. of a mol of the metavanadate, and, after reduction with sulphur dioxide, evaporating in a current of sulphur dioxide. Blue crystals of **ammonium trivanadyl disulphite,** $(NH_4)_2O.3VO_2.2SO_2.H_2O$, were formed; and in an analogous manner **sodium trivanadyl disulphite,** $Na_2O.3VO_2.2SO_2.4H_2O$; **potassium trivanadyl disulphite,** $K_2O.3VO_2.2SO_2$; and **zinc trivanadyl disulphite,** $ZnO.3VO_2.2SO_2$, were prepared. The green salts were obtained by reducing a soln. of a metavanadate, adding ammonium sulphite and evaporating the liquor. In this way, **ammonium vanadyl disulphite,** $(NH_4)_2O.VO_2.2SO_2.2H_2O$; **sodium vanadyl disulphite,** $Na_2O.VO_2.2SO_2.5H_2O$; and **potassium vanadyl disulphite,** $K_2O.VO_2.2SO_2.5\frac{1}{2}H_2O$, were prepared.

G. Gain obtained **ammonium hexavanadyl tetrasulphite,** $(NH_4)_2O.6VO_2.4SO_2.4H_2O$, in black, elongated crystals, by mixing ammonium hydrosulphite with the blue soln. obtained by treating ammonium vanadate with a sat. soln. of sulphurous acid, and evaporating at a low temp. in vacuo. He also obtained in an analogous manner **lithium divanadyl hexasulphite,** $5Li_2O.2VO_2.6SO_2.8H_2O$, as a blue crust of microscopic crystals; **sodium decavanadyl hexasulphite,** $Na_2O.10VO_2.6SO_2.2H_2O$, in black crystals; **potassium hexavanadyl tetrasulphite,** $K_2O.6VO_2.4SO_2.5H_2O$, in blue crystals; **rubidium divanadyl trisulphite,** $2Rb_2O.2VO_2.3SO_2.2H_2O$, in slender needles or as a grey crystalline powder; **cæsium divanadyl tetrasulphite,** $3Cs_2O.2VO_2.4SO_2.8H_2O$, resembling the rubidium salt; and **thallium hexavanadyl tetrasulphite,** $Tl_2O.6VO_2.3SO_2.8H_2O$, or $Tl_2SO_3.3(VO)_2SO_3.8H_2O$.

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§ 23. Sulphites of the Selenium-Uranium Family

The possible existence of **selenium sulphite**, $SeSO_3$, is discussed in connection with selenium sulphotrioxide; and the corresponding tellurium sulphite, $TeSO_3$, is discussed in connection with **tellurium sulphotrioxide.** H. Berglund[1] prepared **ammonium tellurium sulphite,** $(NH_4)_2SO_3.TeSO_3.nH_2O$, soluble in water.

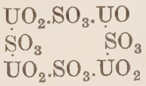
A. Moberg[2] reported **chromous sulphite**—presumably $CrSO_3$—to be formed, as a brick-red precipitate, when aq. soln. of chromous chloride and potassium sulphite are mixed. The precipitate should be washed away from access of air; it becomes brown in a few days owing to its gradual conversion into bluish-green basic chromic sulphite. This change is hastened in air. L. N. Vauquelin prepared normal **chromic sulphite**—presumably $Cr_2(SO_3)_3$—when chromic hydroxide is dissolved in sulphurous acid; or, according to M. Prud'homme, in a soln. of sodium hydrosulphite. G. Scutari-Manzoni obtained it by warming on a water-bath a mixture of molar proportions of powdered chrome-alum and sodium sulphite with just enough water to dissolve the mixture. On cooling the soln. sodium sulphate crystallizes out. The green liquid was found by J. S. Muspratt to give a greenish-white precipitate when treated with alcohol; and P. Berthier found that when the soln. is boiled, a basic salt is precipitated. The cold soln. does not give a precipitate with potassium carbonate, or sodium hydroxide, but precipitation is complete when the soln. is boiled. Similar results were obtained with ammonia, and the soln. then has a light red colour. When a soln. of the normal salt is boiled, P. Berthier, and J. Danson observed the separation of **chromic trioxysulphite,** $Cr_2O_3.Cr_2(SO_3)_3.16H_2O$; and A. Röhrig obtained a similar precipitate by the addition of alcohol. The green powder is decomposed when heated. K. Seubert and M. Elten obtained **chromic tetrahydroxysulphite,** $3Cr_2O_3.3SO_2.3H_2O$, or $Cr_2(SO_3)_2.4Cr(OH)_3.6H_2O$, or $Cr_2(OH)_4SO_3.2H_2O$, as a green precipitate, by mixing $0{\cdot}05N$- or $0{\cdot}1N$-soln. of sodium sulphite and chromic chloride as nearly neutral as possible, and boiling. A. Recoura mixed aq. soln. of a mol. of chromic sulphate and 3 mols. of sodium sulphite, and obtained a green colloidal soln. which is flocculated, on boiling, to form a green precipitate of **chromium pentoxysulphite,** $2Cr_2O_3.SO_2$, or $Cr_2O_3.Cr_2O_2(SO_3)$. It may be that the alkali sulphite forms a complex salt in the unboiled soln. By evaporating the mother-liquor, **chromic dioxysulphite,** $Cr_2O_3(SO_3)$, is formed as a green mass which yields a green colloidal soln. with water. The reaction in the original soln. is probably that symbolized:

$$Cr_2(SO_4)_3+3Na_2SO_3=Cr_2O_2.SO_3+2SO_2+3Na_2SO_4.$$

The chromium in the cold soln. is marked from attack by many reagents. Thus, if 6 mols. of ammonia in aq. soln. be added to a soln. containing a mol. of chromic sulphate and 3 mols. of sodium sulphite, chromic hydroxide begins to separate out in 5 min.; if 6 mols. of sodium sulphite are present, the precipitation begins in 10 min.; if 9 mols., in 12 hrs.; and if 15 mols. are present, no precipitate is formed. E. Berglund found that chromic hydroxide dissolves freely in an aq. soln. of potassium sulphite, and on evaporating the green liquid, a gelatinous mass is obtained. He made **potassium chromic oxysulphite,** $K_2O.Cr_2O_3.2SO_2.nH_2O$, or $KCrO(SO_3)$, as a green precipitate, by mixing a soln. of chromic salt and potassium sulphite, and after the mixture has stood for some time, washing the precipitate. It decomposes if the washing be long continued.

In the absence of other acids, E. Péchard found that sulphurous acid does not reduce molybdates, but forms a series of complex salts. Thus, if sulphur dioxide be passed into a conc. soln. of ordinary ammonium molybdate until the liquid smells strongly of the gas, colourless, microscopic, doubly-refracting octahedra of **ammonium decamolybdatotrisulphite,** $4(NH_4)_2O.10MoO_3.3SO_2.6H_2O$, are formed. It begins to decompose at ordinary temp., and when heated to 440°, gives off sulphur dioxide, ammonia, and water. The salt is sparingly soluble in water. A. Rosenheim held that the formula of the compound prepared in this manner is that of **ammonium octomolybdatodisulphite,** $3(NH_4)_2O.8MoO_3.2SO_2.5H_2O$. A. Rosenheim obtained white needles of **ammonium pentamolybdatodisulphite,** $2(NH_2)_2O.5MoO_3.2SO_2.12H_2O$, by supersaturating with sulphur dioxide a cold soln. of sodium paramolybdate mixed with ammonium chloride. E. Péchard obtained plates of **sodium decamolybdatotrisulphite,** $4Na_2O.10MoO_3.3SO_2.12H_2O$, by evaporating in vacuo a soln. of sodium molybdate, sat. with sulphur dioxide; the evaporation of the mother-liquor gives octahedral crystals of the *hexadecahydrate.* A. Rosenheim obtained **sodium pentamolybdatodisulphite,** $2Na_2O.5MoO_3.2SO_2.8H_2O$; but he did not succeed in making **lithium pentamolybdatodisulphite.** E. Péchard obtained by the method just indicated, amber coloured, prismatic crystals of **potassium decamolybdatotrisulphite,** $4K_2O.10MoO_3.3SO_2.10H_2O$; and if potassium bromide be added to a soln. of ammonium molybdate, sat. with sulphur dioxide, yellow needles of **ammonium potassium decamolybdatotrisulphite,** $4K(NH_4)O.10MoO_3.3SO_2.9H_2O$, are formed. A. Rosenheim regarded the potassium salt just indicated as **potassium pentamolybdatodisulphite,** $2K_2O.5MoO_3.2SO_2.H_2O$; and he also made **rubidium pentamolybdatodisulphite,** $2Rb_2O.5MoO_3.2SO_2.\frac{1}{2}H_2O$; and **cæsium pentamolybdatodisulphite,** $2Cs_2O.5MoO_3.2SO_2.6H_2O$. E. Péchard tried to make a **barium decamolybdatotrisulphite** by adding barium chloride to one of the alkali salts, but found that sulphur dioxide was given off, and the product obtained was a mixture of variable proportions of barium molybdatosulphite and molybdate; but A. Rosenheim made **barium pentamolybdatodisulphite,** $2BaO.5MoO_3.2SO_2.10H_2O$; and **strontium pentamolybdatodisulphite,** $2SrO.5MoO_3.2SO_2.12H_2O$. G. Canneri and L. Fernandes obtained minute prisms of **rare-earth molybdatosulphites** by saturating a conc. soln. of ammonium paramolybdate with sulphur dioxide, and adding a rare-earth acetate. The composition of the crystals varied on fractional crystallization, the rare-earth content thus became smaller and smaller. It was not possible to assign rational formulæ to the products, and it was suggested that this is due to the partial miscibility in the solid state of ammonium molybdatosulphite with the corresponding rare-earth compounds.

C. F. Rammelsberg prepared **uranous oxysulphite,** $UO.SO_3.2H_2O$, or $U(OH)_2SO_3.H_2O$, by the action of sodium sulphite on an aq. soln. of uranium tetrachloride, some sulphur dioxide is evolved, and the greyish-green precipitate is dried over sulphuric acid; O. Brunck obtained this basic salt by boiling the soln. of the normal salt—presumably **uranium disulphite,** $U(SO_3)_2$—obtained by adding an excess of sodium hydrosulphite to a soln. of a uranyl salt. The reddish-brown precipitate passes into soln. The basic salt loses water and sulphur dioxide when heated and forms the tritoctoxide. It is insoluble in water, and easily soluble in sulphurous acid. Uranyl hydroxide itself, said A. Girard, is not soluble in liquid sulphur dioxide. A. Remelé, J. S. Muspratt, and P. Berthier obtained a yellow precipitate by boiling a soln. of ammonium uranyl carbonate in sulphurous acid, or a uranyl salt with a soln. of ammonium sulphite, and obtained what J. S. Muspratt regarded as normal uranyl sulphite, but what A. Girard considered to be uranyl oxysulphite, and L. Scheller, ammonium uranyl oxysulphite. K. Seubert and M. Elten obtained orange **uranyl hexahydroxypentasulphite,** $3UO_2(OH)_2.5(UO_2)SO_3.10H_2O$, by mixing hot *N*-soln. of uranyl nitrate and sodium sulphite; and washing the precipitate with alcohol, since water makes it gelatinous. V. Kohlschütter prepared anhydrous **uranyl sulphite,** $(UO_2)SO_3$, by heating the hydrate at 105°. Its constitutional formula is represented by



$$\begin{array}{ccc} UO_2.SO_3.UO \\ SO_3 \qquad SO_3 \\ UO_2.SO_3.UO_2 \end{array}$$

J. S. Muspratt, and A. Girard prepared the *tetrahydrate*, $(UO_2)SO_3.4H_2O$, or $UO_2(OH)(HSO_3)$, by passing sulphur dioxide into water with F. J. Malaguti's uranium hydroxide in suspension, and evaporating the yellow soln. spontaneously. A. Röhrig obtained it by treating uranyl acetate with sulphurous acid; V. Kohlschütter, by passing sulphur dioxide into a soln. of uranyl acetate; K. Seubert and M. Elten, by mixing cold, normal soln. of uranyl nitrate and sodium sulphite, and passing sulphur dioxide into the filtrate, and adding an equal vol. of alcohol for precipitation; and H. Lienau, by boiling L. Scheller's ammonium salt—*vide infra.* The salt is variously described as forming yellow prisms, or needles. It is stable at ordinary temp., and when dried on a water-bath was found by V. Kohlschütter to form a golden-yellow mass of prismatic crystals of the *tritahenahydrate*, $(UO_2)SO_3.2\frac{3}{4}H_2O$. A. Girard said that the sulphite forms uranyl oxide at a low temp.; and at a higher temp. the tritoctoxide is formed. The salt is insoluble in water; soluble in aq. or alcoholic sulphurous acid, and is precipitated from this soln. by boiling, or by alkali sulphites. A. Röhrig said that **uranyl hydrosulphite** does not exist; V. Kohlschütter said that an acid salt may exist in soln.

V. Kohlschütter reported **ammonium tetrauranyl pentasulphite,** $(NH_4)_2(UO_2)_4(SO_3)_5$, to be formed by treating a soln. of uranyl nitrate with an acid soln. of ammonium hydrosulphite, and stirring the washed precipitate with sulphurous acid on a water-bath until a drop of the soln. deposits tabular crystals. V. Kohlschütter also prepared **sodium tetrauranyl pentasulphite,** $Na_2(UO_2)_4(SO_3)_5.nH_2O$; and **potassium tetrauranyl pentasulphite,** $K_2(UO_2)_4(SO_3)_5$; **ammonium triuranyl disulphite,** $(NH_4)_2O.3UO_3.2SO_2$, by warming the filtrate containing much sulphur dioxide, obtained in preparing the preceding salt, until the sulphur dioxide is almost all expelled. It is also made by mixing a 10 per cent. soln. of uranyl nitrate and ammonium hydrosulphite so that the molar ratio $UO_2:(NH_4)HSO_3$ is 1 : 4 to 6; on warming the mixture on the water-bath, as sulphur dioxide escapes the salt gradually separates in tabular crystals. V. Kohlschütter also prepared **sodium triuranyl disulphite,** $Na_2O.3UO_3.2SO_2$; and **potassium triuranyl disulphite,** $K_2O.3UO_3.2SO_2$; and he made **ammonium diuranyl trisulphite,** $(NH_4)_2(UO_2)_2(SO_3)_3$, by the method employed by L. Scheller for the hydroxysulphite; by mixing a sulphurous acid soln. of uranyl sulphite, warmed on a water-bath, with ammonium hydrosulphite; by treating ammonium hydrosulphite with a soln. of uranyl nitrate; and by passing sulphur dioxide into a soln. of ammonium uranyl disulphite. V. Kohlschütter made **sodium diuranyl trisulphite,** $Na_2(UO_2)_2(SO_3)_3$, and **potassium diuranyl disulphite,** $K_2(UO_2)_2(SO_3)_2$, in a similar way. The constitution is supposed to be $KSO_3.UO_2.O.SO.O.UO_2.KSO_3$. He also prepared **ammonium uranyl disulphite,** $(NH_4)_2(UO_2)(SO_3)_2$, by passing a current of sulphur dioxide into a soln. of uranyl nitrate and an excess of ammonia, and allowing the feeble acidic soln. to stand for a day—if the sulphur dioxide be passed for too long a time, the diuranyl trisulphate is formed. It is also prepared by mixing an excess of ammonium hydrosulphite with a soln. of uranyl nitrate, and allowing the mixture to stand for some time when the voluminous precipitate forms a mass of yellow crystalline plates. F. L. Hahn and co-workers prepared the ammonium uranyl sulphite by the method used for the corresponding copper complex. V. Kohlschütter also made **sodium uranyl disulphite,** $Na_2(UO_2)(SO_3)_2$; and **potassium uranyl disulphite,** $K_2(UO_2)(SO_3)_2$, in an analogous way. L. Scheller reported **ammonium uranyl hydroxysulphite,** $(NH_4)(OH)(UO_2)SO_3.nH_2O$, as a yellow powder by mixing soln. of uranyl sulphite and ammonium hydrosulphite. H. Lienau could not obtain it in this way. L. Scheller said that the salt is not soluble in water, but is more soluble than the potassium or ammonium salts in sulphurous acid. The corresponding **sodium uranyl hydroxysulphite,** $Na(OH)(UO_2)(SO_3)$, and **potassium uranyl hydroxysulphite,** $K(OH)(UO_2)(SO_3)$, were also prepared by L. Scheller. H. Lienau obtained the uranyl sulphite of A. Girand by this process; and V. Kohlschütter, the potassium diuranyl trisulphite.

The rare-earth metals of the cerium group, by virtue of their high basicity, combine with complex acid radicals to form compounds analogous to those of the alkali and alkaline-earth metals. In these compounds the individuality of the complex is not destroyed by the physical and chemical characteristics of the rare earths. G. Canneri and L. Fernandes obtained uranyl sulphites of the general formula $R_2(UO_2)_5(SO_3)_8.15H_2O$ by crystallizing in vacuo at the ordinary temp. a soln., saturated with sulphur dioxide, containing the rare-earth hydroxide and uranyl sulphate. The products obtained were microcrystalline and of constant composition. They suggested the constitution

$$SO_3 : R.SO_3.UO_2.SO_3.UO_2.SO_3.UO_2.SO_3.UO_2.SO_3.UO_2.SO_3R : SO_3.$$

The following salts were so prepared, **cerium uranyl sulphite,** $Ce_2(UO_2)_5(SO_3)_8.15H_2O$; **lanthanum uranyl sulphite,** $La_2(UO_2)_5(SO_3)_8.15H_2O$; **praseodymium uranyl sulphite,** $Pr_2(UO_2)_5(SO_3)_8.15H_2O$; and **neodymium uranyl sulphite,** $Nd_2(UO_2)_5(SO_3)_8.15H_2O$.

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§ 24. Sulphites of the Manganese and Iron Families

J. Meyer[1] treated manganese dioxide in a similar manner, in boiling water, and obtained a mixture of manganese dithionate, sulphate, and sulphite: $2MnO_2+3H_2SO_3=Mn_2(SO_3)_3+3H_2O+O$; $Mn_2(SO_3)_3=MnSO_3+MnS_2O_6$; and $MnSO_3+O=MnSO_4$. The **manganic sulphite,** $Mn_2(SO_3)_3$, first formed is not stable and is rapidly decomposed, forming normal **manganese sulphite,** $MnSO_3$. and the dithionate. J. F. John passed an excess of sulphur dioxide into water with manganese carbonate in suspension and obtained a soln. of manganese sulphite, $MnSO_3$. P. Berthier boiled the liquid during the passage of the gas and obtained a precipitate of the *hemipentahydrate*, $MnSO_3.2\frac{1}{2}H_2O$. J. S. Muspratt allowed the liquid sat. with sulphur dioxide to stand for some time to permit the hemipentahydrate to deposit. C. F. Rammelsberg obtained the same hydrate by the action of manganese acetate on sodium sulphite; and A. Röhrig, by treating an acidic soln. with alcohol, or evaporating the liquid. No evidence of the formation of **manganese hydrosulphite,** $Mn(HSO_3)_2$, was observed; although G. Denigès obtained a complex salt with aniline, $Mn(HSO_3)_2.2C_6H_5NH_2$; and manganese sulphite can also be prepared by the action of sulphur dioxide on water with manganese sulphide in suspension. W. E. Henderson and H. B. Weiser observed that the manganese sulphite first precipitated passes into soln. as hydrosulphite as the current of gas is continued—*vide infra,* ferrous sulphite. The white, crystalline powder of the hemipentahydrate, according to J. S. Muspratt, appears at first to be tasteless, but afterwards, it develops an offensive, metallic taste. Analyses were made by J. F. John, C. F. Rammelsberg, and A. Röhrig. J. S. Muspratt obtained $MnSO_3.2H_2O$; and A. Gorgeu considered the hemipentahydrate to be a mixture of the mono- and tri-hydrates. J. F. John reported that the salt is permanent in air, and is insoluble in water—F. Heeren and P. Berthier said sparingly soluble—and insoluble in alcohol; J. S. Muspratt said that it is insoluble in ether; and P. Berthier, freely soluble in sulphurous acid, and other acids. A. Naumann found it to be insoluble in acetone. J. F. John reported that the salt is decomposed by heat; J. S. Muspratt, that at 100° it loses water without further decomposition; and with stronger heating in air gives off sulphur dioxide and forms manganese trioxide. C. F. Rammelsberg observed that in a retort, water and sulphur dioxide are given off, and a greenish-brown residue of manganese sulphide, trioxide, and sulphate is formed. According to A. Gorgeu, if in preparing the trihydrate, the soln. are worked at 100°, the *monohydrate,* $MnSO_3.H_2O$, is formed; and G. Denigès obtained the same hydrate by boiling manganese aniline hydrosulphite in water. The rhombic prisms of the monohydrate lose their water at 150°. The salt is not stable in the mother-liquid; and in water—and especially in the presence of sulphurous acid—it forms the *trihydrate,* $MnSO_3.3H_2O$, in a few minutes. K. Seubert and M. Elten obtained the trihydrate by mixing soln. of manganese sulphate and sodium sulphite at ordinary temp. G. Denigès said that it is best to work with a soln. containing acetic acid, which, when allowed to stand for 24 hrs., yields crystals of the trihydrate. A. Wächter obtained the trihydrate by the method indicated for preparing the hemipentahydrate. According to A. Gorgeu, the trihydrate can be obtained in monoclinic crystals by the evaporation at ordinary temp. of a soln. of manganese sulphite in a conc. aq. soln. of sulphurous acid, or of a soln. obtained by adding an alkaline sulphite to a large excess of a soln. of a manganese salt until a permanent precipitate just begins to form. This salt has a pale rose colour; it dissolves in 10,000 parts of cold or 5000 parts of hot water; is rather more soluble in conc. soln. of manganous salts; and dissolves somewhat easily in a conc. aq. soln. of sulphurous acid. It oxidizes slowly in dry air, more quickly in ordinary air, and rapidly in moist air or in contact with aerated water, especially if finely powdered. In presence of water, chlorine, bromine, and iodine convert it into sulphate. The trihydrate begins to lose water at 70°, and oxidizes somewhat rapidly. When calcined at a bright red-heat, it leaves a residue of trimanganese tetroxide. The mono- and tri-hydrates when heated out of contact with air give off sulphur dioxide and leave a residue of manganese monoxide, sulphate, and sulphide. Heated gradually to redness in a current of hydrogen, manganese sulphite leaves a residue of 87 parts manganese monoxide and 13 parts manganese sulphide. P. Ray and B. K. Goswami obtained **manganous hydrazinodihydrosulphite,** $Mn(HSO_3)_2.N_2H_4$, by the action of a soln. of manganese sulphite in an excess of sulphurous acid, on a dil. soln. of hydrazine hydrate; the white, crystalline precipitate is washed with alcohol, and then with ether, and dried over sulphuric acid in vacuo. If a conc. soln. of hydrazine hydrate is used, the white precipitate first formed changes into manganous hydroxide, which quickly oxidizes in air.

K. Seubert and M. Elten prepared rose-coloured, *octohydrated* **manganese tetrahydroxypentasulphite,** $2Mn(OH)_2.5MnSO_3.8H_2O$, by heating a mixture of *N*-soln.

of manganese and sodium sulphites, and washing the product with hot water; and by using 0·1N-soln., he obtained the *henahydrate*, $2Mn(OH)_2.5MnSO_3.11H_2O$. A. Gorgeu prepared **manganese dihydroxydisulphite,** $2MnSO_3.Mn(OH)_2.2H_2O$, by slowly mixing a large excess of a 3–5 per cent. soln. of sodium or potassium sulphite with a boiling 20–25 per cent. soln. of manganese sulphate. The white precipitate forms a rose-coloured, crystalline powder consisting of rhombic prisms which are decomposed by a prolonged washing. The salt loses no water at 200°, but is decomposed at a higher temp.

H. Berglund made **ammonium manganous sulphite,** $(NH_4)_2SO_3.MnSO_3$, as a crystalline powder, by mixing soln. of the component salts; and A. Gorgeu, from a soln. of manganese sulphite in a 15–20 per cent. soln. of ammonium sulphite sat. with sulphur dioxide, by evaporating the liquid on a water-bath or over a medium which will absorb sulphur dioxide. The rectangular prisms mixed with six-sided prisms are more stable towards oxygen than the potassium or sodium salt, and are less readily affected by water. When heated out of contact with air, ammonia is first evolved, then ammonium hydrosulphite, and finally sulphur dioxide, and a mixture of manganese oxide and sulphide remains. F. L. Hahn and co-workers prepared the ammonium manganese sulphite by the method used for the ammonium copper complex salt. A. Gorgeu prepared **sodium manganous sulphite,** $Na_2SO_3.MnSO_3.H_2O$, in monoclinic prisms, from a soln. of sodium sulphite and hydrosulphite, saturated in the cold, and then heated to 80° and mixed with a 20 per cent. soln. of $MnCl_2$. The crystals are dried on a porous tile. The crystals are rapidly decomposed into the component salts by hot or cold water, and at 150° lose their water of crystallization. If the soln. of sodium sulphite used be mixed with half its vol. of water, **sodium manganous pentasulphite,** $Na_2SO_3.4MnSO_3$, is formed. It is only slightly attacked by water. F. L. Hahn and co-workers prepared the sodium and potassium complex salts by the method used for the complex copper salts. A. Gorgeu prepared **potassium manganous sulphite,** $K_2SO_3.MnSO_3$, by the method employed for the corresponding ammonium salt, but if the evaporation be conducted on a water-bath, needle-like crystals of **potassium manganous trisulphite,** $K_2SO_3.2MnSO_3$, are formed. G. Canneri prepared **thallous manganous sulphite,** $Tl_2Mn(SO_3)_2$, as a white, microcrystalline powder.

When iron is dissolved in sulphurous acid out of contact with air, C. L. Berthollet, M. J. Fordos and A. Gélis, and A. Vogel showed that crystals of **ferrous sulphite,** $FeSO_3.3H_2O$(or $2\frac{1}{2}H_2O$), are deposited—either immediately, or on evaporation out of contact with air—before the crystals of thiosulphate appear: $2Fe+3H_2SO_3=FeSO_3+FeS_2O_3+3H_2O$. A little sulphur, and iron sulphide are formed at the same time. No hydrogen is given off, for it is apparently consumed in reducing the sulphite to thiosulphate. C. J. Koene separated the two salts by washing the crystals with alcohol—the thiosulphate dissolves, the sulphite is insoluble. K. Seubert and M. Elten observed that ferrous sulphite is formed by the interaction of soln. of a ferrous salt and sodium sulphite, and when ferrous hydroxide is dissolved in sulphurous acid out of contact with air. A red soln. shows that some oxidation has occurred—possibly by dissolved oxygen—but the colour soon disappears, and crystals of the salt are obtained by evaporating the liquid. According to W. E. Henderson and H. B. Weiser, when sulphur dioxide is passed into ice-cold water in which ferrous sulphide is suspended, out of contact with air, ferrous sulphite is deposited as a crystalline powder, in accord with a suggestion by A. Guerout: $FeS+H_2SO_3=FeSO_3+H_2S$; if the current of gas be continued, the crystals dissolve, and a soln. of ferrous hydrosulphite, $Fe(HSO_3)_2$, is formed. If the soln. be warmed, crystals of the normal sulphite are again deposited. C. F. Rammelsberg said that a stream of sulphur dioxide passed into water with manganese sulphide in suspension forms thiosulphate and sulphur. W. E. Henderson and H. B. Weiser showed that these products are due to a secondary reaction; for the soln. still contains the metal when all the sulphite has been precipitated by boiling, and when treated with acids, it gives the reaction for thiosulphates—liberation of milk of sulphur. In the primary reaction, most of the hydrogen sulphide escapes, but part reacts with sulphur dioxide, forming a very active form of sulphur which unites with the hydrosulphite in soln. to form a thiosulphite, as in H. Debus' reaction : $Fe(HSO_3)_2+S=FeS_2O_3+H_2O+SO_2$. When ferrous sulphite is heated, M. J. Fordos and A. Gélis, and P. Berthier observed that sulphur dioxide and water are evolved, and a black residue is formed. The moist crystals oxidize in air, and the aq. soln. acquires a deep red colour by oxidation. Alkalies precipitate ferrous hydroxide from an aq. soln. of ferrous sulphite. The salt dissolves sparingly in water, and freely in sulphurous acid ; J. S. Muspratt said that the salt is insoluble in alcohol. H. Berglund prepared **ammonium ferrous sulphite,** $(NH_4)_2SO_3.FeSO_3.nH_2O$, from a soln. of the component salts. F. L. Hahn and co-workers prepared the ammonium salt by the method used for the ammonium copper sulphite. G. Canneri prepared **thallous ferrous sulphite,** $Tl_2Fe(SO_3)_2$, as a brick-red, microcrystalline powder.

According to P. Berthier, freshly precipitated ferric hydroxide readily dissolves in sulphurous acid, and the soln. which is red at first soon decolorizes owing to the formation of ferrous sulphate. H. C. H. Carpenter said that the purified and well-washed ferric hydroxide dissolves very slowly, forming a yellow soln. P. Berthier also found that the dried hydroxide dissolves slowly in cold sulphurous acid, but the hot acid dissolves it quickly, forming ferrous sulphate—A. Gélis said ferrous dithionate and sulphite : $Fe_2(SO_3)_3=FeSO_3+FeS_2O_6$; and H. J. Buignet represented the reaction : $Fe_2(SO_3)_3=FeSO_4+FeSO_3+SO_2$. Hence **ferric sulphite,** $Fe_2(SO_3)_3$, has not been isolated, and it is known only as an unstable, red soln. which can be prepared as just indicated, or by the action of sodium sulphite on a soln. of ferric chloride. By working with well-cooled liquids, a neutral soln. can be obtained containing neither a ferrous salt nor sulphurous acid. According to C. J. Koene, A. Gélis, and J. S. Muspratt, **ferric octoxysulphite,** $2Fe_2O_3.Fe_2O_2(SO_3).7H_2O$, is formed, as an ocreous powder, when the red soln. of ferric sulphite is evaporated ; if the soln. of ferric hydroxide in ice-cold sulphurous acid be filtered into 90 per cent. alcohol, and washed with water, the trioxytrisulphite passes into **ferric dioxysulphite,** $Fe_2O_2(SO_3).6H_2O$; and if the red soln. be treated with alcohol, yellowish-brown **ferric trioxytrisulphite,** $Fe_2O_3.Fe_2(SO_3)_3.3H_2O$, is formed. K. Seubert and M. Elten also prepared this basic salt ; and they obtained **ferric heptohydroxysulphite,** $Fe(OH)(SO_3).2Fe(OH)_3$, or $2Fe_2(SO_3)_3.7Fe_2(OH)_6$, as a brownish-yellow, amorphous precipitate by keeping in a warm place a mixture of N- or $0·1N$-soln. of ferric chloride and sodium sulphite.

J. S. Muspratt reported **potassium ferric dioxytrisulphite,** $Fe_2O_2(SO_3).2K_2SO_3.5H_2O$, to be formed as a yellow, crystalline precipitate by adding potash-lye to the red soln. of ferric sulphite ; and C. J. Koene, **potassium ferric dioxydihydrotrisulphite,** $Fe_2O_2(SO_3).2KHSO_3.H_2O$, as a yellow precipitate. The chemical individuality of these basic salts cannot be regarded as established. H. Berglund prepared **potassium ferrosic sulphite,** $2K_2SO_4.FeSO_3.(FeO)_2SO_3$, as a precipitate ; and A. Stromeyer obtained **sodium cuprous ferrosic sulphite,** $Na_2O.Cu_2O.2FeO.Fe_2O_3.6SO_3.16H_2O$, in a similar manner ; the salt was said to be soluble in cold dil. sulphuric and hydrochloric acids with a residue of cuprous chloride ; 100 parts of water dissolve about 0·1 part of the salt.

K. A. Hofmann prepared a series of six **ferrisulphatosulphites ;** thus, **potassium ferrisulphatosulphite,** $KFe(SO_4)SO_3$, or $KSO_4.Fe:SO_3$, was obtained by treating finely powdered iron ammonium alum with potassium hydrosulphite ; it crystallizes in slender, doubly-refracting needles. It is but sparingly soluble in cold water, and the soln. contains ferric salt only. When heated for some time with water at 80°–90°, ferrous sulphate and potassium sulphate are dissolved, and a yellow residue is obtained which is soluble with difficulty in dil. acids with evolution of sulphurous anhydride. It dissolves readily in cold, dil. hydrochloric acid, and the bright yellow soln. gives a blue precipitate with potassium ferrocyanide, and only after boiling, a blue one with potassium ferricyanide. The corresponding **ammonium**

ferrisulphatosulphite, $(NH_4)Fe(SO_4)SO_3$, was obtained by treating ammonium alum with ammonium or sodium hydrosulphite; it crystallizes in slender, yellow needles, is only very slightly soluble in cold and hot water, and by prolonged boiling with water is converted into a red powder, with evolution of sulphur dioxide. It is easily soluble in cold, dil. hydrochloric acid with evolution of sulphur dioxide. When treated with ammonia or dil. alkali-lye, it is decomposed with formation of a brown, flocculent precipitate. Likewise, **potassium ferrisulphatodisulphite,** $K_3Fe(SO_3)_2.SO_4$, or $KSO_4.Fe(KSO_3)_2$, was prepared by digesting the heptanitrososulphonate for about a month with sodium hydrosulphite at 4°. It crystallizes in beautiful, lustrous, dark yellow leaflets, is almost insoluble in cold water, and behaves like the sulphatotetrasulphite when boiled with water or dil. acid; and **sodium ferrisulphatodisulphite,** $Na_3Fe(SO_3)_2SO_4.6H_2O$, by digesting sodium iron heptanitrososulphonate with sodium hydrosulphite for some days. It crystallizes in lustrous, flat, yellow prisms, and is very similar to the corresponding potassium salt. Further, **potassium diferrisulphatotetrasulphite,** $K_4Fe_2(SO_4)(SO_3)_4.5H_2O$, or $(KSO_3)_2 : Fe.SO_3Fe : (KSO_3).5H_2O$, is obtained by treating potassium iron heptanitrosulphonate, $KS_3Fe_4(NO)_7$, dissolved in alcohol with a soln. of sodium hydrosulphite, and allowing the mixture to remain at the ordinary temp. for about 14 days. It forms a yellow, lustrous mass of microscopic needles, is insoluble in cold water, and when boiled with water is decomposed into ferric hydroxide and a soluble ferrous salt. It dissolves immediately in 20 per cent. hydrochloric acid, and the soln. gives a blue precipitate with potassium ferrocyanide, and only a brown coloration with potassium ferricyanide, whence it is concluded that the compound is a ferric salt. On boiling the hydrochloric acid soln., partial reduction of the ferric salt takes place. The corresponding **sodium diferridihydrosulphatotetrasulphite,** $Na_2H_2Fe_2(SO_4)(SO_3)_4.2H_2O$, was obtained by dissolving freshly prepared ferric hydroxide in a conc. soln. of sodium hydrosulphite and sulphurous acid. On evaporating the soln. over sulphuric acid, a red, amorphous substance separates at first; but after this has been removed, a crystalline mixture of the salt together with the sulphatodisulphite is obtained. It can be separated by treating the mixed crystals with a soln. of sodium hydrosulphite, and crystallizes in bright olive-green needles.

J. S. Muspratt[2] found that cobalt carbonate dissolves readily in sulphurous acid, and when the soln. is treated with alcohol, a brownish-red flocculent precipitate of **cobaltous sulphite**—probably $CoSO_3.H_2O$—is formed. According to A. Röhrig, it is probably $CoSO_3.5H_2O$. J. S. Muspratt, and A. Röhrig passed sulphur dioxide into water with cobalt hydroxide in suspension, in the absence of air, and boiled the liquid. The resulting red crystals were those of the pentahydrate, $CoSO_3.5H_2O$. If the soln. be evaporated in a current of hydrogen, C. F. Rammelsberg, and A. Röhrig found that red crystals of the trihydrate, $CoSO_3.3H_2O$, were formed. C. F. Rammelsberg said that much sulphur dioxide is given off during the evaporation. J. Mai and M. Silberberg found that an orange-coloured salt is produced when cobaltous sulphite is treated with potassium cyanide. C. F. Rammelsberg, A. Röhrig, and P. Berthier found that when a neutral soln. of a cobalt salt and potassium sulphite is boiled, part of the cobalt is precipitated as a basic salt which becomes more basic when it is washed with water. K. Seubert and M. Elten saturated a soln. of 23·7 grms. of cobalt chloride, and 12·58 grms. of sodium sulphite with sulphur dioxide; the precipitate first formed dissolved and when the liquid was warmed, a rose-coloured precipitate was produced. **Cobalt dihydroxypentasulphite,** $Co(OH)_2.5CoSO_3.10H_2O$, which, in an atm. of hydrogen, could be washed with water and alcohol without change. If the soln. in an atm. of hydrogen in a sealed tube be heated on a water-bath, rose-coloured **cobalt dihydroxydecasulphite,** $Co(OH)_2.10CoSO_3.5H_2O$, is formed.

H. Berglund prepared **ammonium cobaltous disulphite,** $(NH_4)_2SO_3.CoSO_3.nH_2O$, from a soln. of cobaltous sulphate saturated with ammonium sulphite. The rose-red precipitate is readily oxidized in air. He also obtained yellow **ammonium cobaltous trisulphite,** $(NH_4)_2SO_3.2CoSO_3.11H_2O$. F. L. Hahn and co-workers prepared the ammonium cobalt salt by the method they used for the ammonium copper salt; and similarly also with the sodium and potassium salts. W. Schultze prepared pale red **potassium cobaltous disulphite,** $K_2SO_3.CoSO_3.H_2O$, by heating a mixed soln. of cobaltous sulphate or chloride and a neutral soln. of potassium sulphite; or by boiling cobaltous hydroxide with an acidic soln. of potassium sulphite. The compound readily oxidizes in air. He prepared **sodium cobaltous disulphite,** $Na_2SO_3.CoSO_3.nH_2O$, in a similar manner. G. Jantsch and K. Abresch prepared **lithium cobaltous trisulphite,** $Li_3[Co(SO_3)_3].4H_2O$, by treating a soln. containing lithium nitrite and cobalt nitrate with acetic acid, and adding the resulting soln. to a boiling soln. of lithium sulphite. The complex salt crystallizes out readily if the soln. is kept at 80° to 90° for a short time. On exposure of the soln. to air, cobaltic hydroxide gradually precipitates. The insoluble potassium cobaltous trisulphite, $K_3[Co(SO_3)_3].6H_2O$, may be obtained by direct precipitation. A soln. of the lithium salt yields no precipitate when treated with cold ammonia soln., whereas with sodium hydroxide soln. all the cobalt is precipitated as hydroxide. The soln. has a very low conductivity and exhibits the Tyndall effect; after ultrafiltration the conductivity remains very small, and the Brownian movement is observable. The true solubility of the complex salt thus appears to be very small. Transport observations indicate the presence in the soln. of the $Co(SO_3)_3'''$ ion. G. Canneri prepared **thallous cobaltous sulphite,** $Tl_2Co(SO_3)_2$, as a pink, microcrystalline powder.

A. Geuther treated freshly prepared cobaltic hydroxide with a warm, conc., aq. soln. of ammonium sulphite. The liquid soon acquires a dark brown colour, and ammonia is given off as the hydroxide dissolves. The liquid presumably contains an unstable **cobaltic sulphite,** $Co_2(SO_3)_3$. A dark reddish-yellow powder soon separates from the soln. K. A. Hofmann and S. Reinsch prepared *pentahydrated* **cobaltic diamminosulphite,** $Co_2(SO_3)_3.2NH_3.5H_2O$, by dissolving cobalt acetate in 7 per cent. aq. ammonia; exposing the soln. to air until it becomes deep violet; saturating the liquid with sulphur dioxide; and washing the brown amorphous precipitate with sulphurous acid. The salt is sparingly soluble in water, and when treated with soda-lye yields cobalt hydroxide; when boiled with 7 per cent. aq. ammonia it is converted into yellow amorphous **cobaltic pentamminosulphite,** $Co_2(SO_3)_3.5NH_3.7H_2O$; K. A. Hofmann and A. Jenny prepared **cobaltic hexamminosulphite,** $Co_2(SO_3)_3.6NH_3.3H_2O$, by passing sulphur dioxide into a filtered ammoniacal soln. of cobalt acetate which had been exposed to air for 72 hrs. The dark brown rhombic prisms are sparingly soluble in water; and give a deep violet colour with sulphuric acid. K. A. Hofmann and S. Reinsch obtained **cobaltic enneamminosulphite,** $Co_2(SO_3)_3.9NH_3.3H_2O$, by passing sulphur dioxide through an ammoniacal soln. of cobalt acetate which has been exposed to air for 2 or 3 days. The brownish-yellow, birefringent needles are soluble in water. P. Ray and B. K. Goswami obtained **cobalt pentitaenneahydrazinosulphite,** $5CoSO_3.9N_2H_4.6H_2O$, by dropping a soln. of cobalt hydrosulphite into a dil soln. of hydrazine hydrate, washing the voluminous, white precipitate with alcohol, and drying it in vacuo over sulphuric acid. The crystalline salt is neutral towards litmus; it is soluble in cold water, and decomposed by boiling water. By mixing an excess of a conc. soln. of hydrazine hydrate with a soln. of cobalt hydrosulphite, a voluminous, flesh-coloured precipitate of **cobalt dihydrazinosulphite,** $CoSO_3.2N_2H_4.H_2O$, is formed. The water is not all expelled at 110°, and the salt decomposes at 125°; it reacts alkaline towards litmus, and is decomposed by boiling water. If the pentitaenneahydrazinosulphite is suspended in water and treated with sulphur dioxide, and yellow soln. slowly evaporated on a water-bath, crystals of **cobalt hemihydrazinosulphite,** $2CoSO_3.N_2H_4.3H_2O$, are formed. These can be washed with alcohol, and dried over sulphuric acid in vacuo. The water is not all expelled at 110°; the salt is neutral toward litmus; and the salt is not decomposed by boiling water. If the dihydrazinosulphite is suspended in water and treated with sulphur dioxide, and alcohol is added to the filtered soln., reddish crystals of **cobalt dihydrazino-**

hydrosulphite, $Co(HSO_3)_2.2N_2H_4.2H_2O$, are formed, The salt is very soluble in water, forming a pale red soln.; it is not completely dehydrated at 120°; it is not decomposed by dissolution in boiling water; and it dissolves in dil. aq. ammonia, forming a soln. which is not decomposed by boiling. If cobalt dihydrazinosulphite be suspended in water, and treated with sulphur dioxide, and alcohol be added to the filtered liquid, a red precipitate of **cobalt hydrazinohydrosulphite,** $Co(HSO_3)_2.N_2H_4.\frac{1}{2}H_2O$, is formed. The salt reacts acidic towards litmus; it is not decomposed by boiling with water; it is slightly soluble in sulphurous acid, and in dil. aq. ammonia. The yellow, ammoniacal soln. is not decomposed when boiled.

A. Geuther, and W. Schultze prepared impure **potassium cobaltic sulphite,** $K_2SO_6.Co_2(SO_3)_3$, or $KCo(SO_3)_2$, by the action of a warm soln. of potassium sulphite on cobaltic hydroxide. The pale brown product is sparingly soluble in water, and freely soluble in sulphurous or hydrochloric acid. The salt blackens in air, and cannot be dried without decomposition. It is also changed by washing with water. The corresponding **sodium cobaltic sulphite,** $Na_2Co_2(SO_3)_2$, was obtained by W. Schultze in an analogous way. F. L. Hahn also prepared what he called **sodium trisulphitocobaltate**—presumably $Na_2[Co(SO_3)_3]$. H. Berglund reported a complex salt, $(NH_4)_2SO_3.2CoSO_3.Co_2(SO_3)_3.14H_2O$, to be formed in yellow crystals by saturating with sulphur dioxide an ammoniacal soln. of cobalt chloride or acetate oxidized by exposure to air. The compound can be regarded as **cobaltous ammonium hexasulphitodicobaltate,** the cobalt salt of **hexasulphitodicobaltic acid,** $H_6[Co_2(SO_3)_6]$, or $H_3[Co(SO_3)_3]$. By treating the soln. of this compound in dil. nitric or hydrochloric acid, with alkali hydroxide, nitrate, acetate, etc. voluminous, insoluble precipitates were obtained representing **ammonium cobaltous hexasulphitocobaltate,** $(NH_4)_4Co[Co_2(SO_3)_6].8H_2O$; **potassium cobaltous hexasulphitodicobaltate,** $K_4Co[Co_2(SO_3)_6]$; **silver hexasulphitodicobaltate,** $Ag_6[Co_2(SO_3)_6]$; **silver cobaltous hexasulphitodicobaltate,** $Ag_4Co[Co_2(SO_3)_6]$; **calcium hexasulphitodicobaltate,** $Ca_3[Co_2(SO_3)_6]$; **barium hexasulphitodicobaltate,** $Ba_3[Co_2(SO_3)_6]$; and **bismuth hexasulphitodicobaltate,** $Bi_2[Co_2(SO_3)_6]$.

G. Vortmann and G. Magdeburg prepared **ammonium cobaltic tetramminodisulphite,** $NH_4Co(NH_3)_4(SO_3)_2.2H_2O$, in small yellow needles; **cobaltosic octamminopentasulphite,** $Co_2Co''_5(NH_3)_8(SO_3)_5.24H_2O$, as a yellow crystalline powder; **ammonium cobaltic tetramminotrisulphite,** $Co(NH_3)_4(NH_4SO_3)_3.5H_2O$, in yellowish-brown needles; **barium cobaltic octamminohexasulphite,** $Ba_3Co_2(NH_3)_8(SO_3)_6.7H_2O$, in golden-yellow scales; **ammonium barium cobaltic octamminohexasulphite,** $(NH_4)_2Ba_2Co_2(NH_3)_8(SO_3)_6.7H_2O$, in golden-yellow scales; and *dodecahydrated* **cobaltic tetramminotrisulphite,** $Co_2(NH_3)_4(SO_3)_3.12H_2O$, in orange crystals, also described by A. Werner and H. Grüger, and A. Werner and A. Klein. Similarly also with the *octodecahydrate*. G. Vortmann and G. Magdeburg also prepared **cobaltic decamminotrisulphite,** $Co_2(NH_3)_{10}(SO_3)_3.4H_2O$, as a reddish-yellow crystalline powder; **sodium cobaltic pentamminotrisulphite**, $Co(NH_3)_5(NaSO_3)_3.H_2O$, in light brown crystals; **cobaltic pentamminotrisulphite,** $Co_2(NH_3)_5(SO_3)_3.4H_2O$, as a brownish-yellow powder; **cobaltic tetramminochlorosulphite,** $Co(NH_3)_4(SO_3)Cl.2H_2O$, in dark brown crystals; **cobaltic sulphitopentamminochloride,** $Co(NH_3)_5(SO_3)Cl$, as a brown crystalline powder; and **cobaltic hexamminochlorosulphite,** $Co(NH_3)_6Cl(SO_3).3H_2O$, in yellow needles.

C. Künzel found that a conc. soln. of cobaltic chloropentamminochloride in dil. ammonia, mixed with ammonium hydrosulphite until the liquor smells neither of ammonia nor sulphur dioxide, passes from a red to a dark yellow colour, and deposits yellow needles of **cobaltic hexamminotrisulphite,** $[Co(NH_3)_6][Co(SO_3)_3].H_2O$. A. Geuther obtained it from cobaltic hydroxide and ammonium sulphite. It was also prepared by K. A. Hofmann and A. Jenny along with aquodisulphitotriamminocobaltic acid. The salt is insoluble in cold water, and is slowly decomposed by boiling water; aq. ammonia has no action in the cold, but when boiled a yellow soln. is slowly formed; and hot soda-lye gives a black precipitate of cobaltic hydroxide. If a very large proportion of ammonium sulphite is used in the preparation, the soln. slowly deposits brown octahedral crystals of **cobaltic bishexamminoenneasulphite,** $[Co(NH_3)_6]_2(SO_3)_3.2Co_2(SO_3)_3.15H_2O$, which acquire a yellow pulverulent film on exposure to air. It is very sparingly soluble in water.

G. Vortmann and G. Magdeburg obtained yellow needles of **cobaltic hexamminochlorosulphite,** $[Co(NH_3)_6]Cl(SO_3).3H_2O$, by passing sulphur dioxide into a hot soln. of the hexamminochloride in dil. ammonia, and allowing the liquid to stand for 12 hrs. It was also made by boiling one part of the hexamminochloride in a soln. of 3 parts of ammonium sulphite, and cooling the liquid.

K. A. Hofmann and S. Reinsch obtained **cobaltic aquopentamminotrisulphite,** $[Co(NH_3)_5H_2O]_2(SO_3)_3.H_2O$, in brownish-yellow, monoclinic plates, along with sparingly soluble ammonium aquotetramminosulphite, by digesting cobaltic carbonatotetramminochloride, or cobaltic aquopentamminochloride, with an ammoniacal soln. of ammonium sulphite, and precipitating with alcohol. The salt forms with fuming hydrochloric acid a brownish-yellow soln., then a red crystalline powder and violet soln.; and with conc. sulphuric acid, a ruby-red soln. is formed. The same salt was made by G. Vortmann and G. Magdeburg; and it may be the same as A. Werner and H. Grüger's sulphitopentamminosulphite. G. Vortmann and G. Magdeburg also reported **sodium cobaltic aquopentamminotrisulphite,** $[Co(NH_3)_5H_2O](NaSO_3)_3$, to be formed by the action of sodium hydrosulphite soln. on an ammoniacal soln. of cobaltic aquopentamminotrichloride, and precipitation with alcohol. It may be A. Werner and H. Grüger's sulphitopentammine. G. Vortmann and G. Magdeburg added sulphurous acid to an ammoniacal soln. of cobalt and ammonium chloride which had been standing for a long time, and obtained a brownish-yellow precipitate of cobaltic aquopentamminotrisulphite, $[Co(NH_3)_5H_2O]\{Co(SO_3)_3\}.4H_2O$. C. Künzel obtained it by passing sulphur dioxide through a dil., ammoniacal soln. of cobaltic chloropentamminochloride; or of cobaltic hexamminotrisulphite, and A. Geuther, by dissolving cobaltic hydroxide in a conc., neutral soln. of ammonium sulphite. The brown salt is insoluble in cold water, is decomposed by hot water; nitric acid yields nitrous fumes; and ammonia gives the corresponding hexammine. E. Hesse also examined this salt. A. Werner and H. Grüger prepared a series of **cobaltic sulphitopentammines,** $[Co(NH_3)_5SO_3]X$; thus, **cobaltic sulphitopentamminosulphite,** $[Co(NH_3)_5SO_3]_2SO_3.2H_2O$, was obtained by adding 10–12 grms. of sodium hydrosulphite to 500 c.c. of a soln. prepared by passing air for 7–8 hrs. through a mixture of 20 grms. of cobalt carbonate in dil. hydrochloric acid, 100 grms. of ammonium carbonate, 500 grms. of water, and 250 grms. conc. aq. ammonia. In 2 or 3 days, crystals of disulphitotetrammine are deposited, and in another 3 days, brown tablets of the sulphitopentammine appear. E. H. Riesenfeld and W. Petrich also prepared this salt. By treating this sulphite with the theoretical quantity of conc. hydrochloric acid, and adding alcohol, **cobaltic sulphitopentamminochloride,** $[Co(NH_3)_5SO_3]Cl$, is formed; it is stable when dry, but unstable in aq. soln., if the sulphitopentamminosulphide be treated with conc. hydrochloric acid, and washed with absolute alcohol, **cobaltic sulphitopentamminohydrodichloride,** $[Co(NH_3)_5SO_3]Cl.HCl$, is formed as a carmine-red, crystalline powder, which, in damp air, quickly passes into the chloride. In an analogous way, **cobaltic sulphitopentamminobromide,** $[Co(NH_3)_5SO_3]Br$, is obtained in brownish-red crystals; and **cobaltic sulphitopentamminonitrate,** $[Co(NH_3)_5SO_2]NO_3$, in brown crystals. P. R. Ray prepared **cobaltic sulphitopentamminothiosulphate,** $[Co(NH_3)_5(SO_3)]_2S_2O_3$, as indicated in connection with the thiosulphate; and on adding alcohol to a soln. of this salt in 5 per cent. soda-lye, **cobaltic hydroxysulphitotetrammine,** $[Co(NH_3)_4(OH)(SO_3)].2H_2O$, was precipitated. K. A. Hofmann and S. Reinsch obtained the trihydrate—*vide infra.* By adding alcohol to the yellow soln. obtained by treating the chloride with sodium hydrosulphite, yellow leaflets of **sodium cobaltic sulphitopentamminotrisulphite,** $[Co(NH_3)_5SO_3]_2SO_3.2Na_2SO_3.H_2O$, are formed.

K. A. Hofmann and S. Reinsch prepared a series of **aquosulphitotetrammines,** $[Co(NH_3)_4H_2O(SO_3)]X$; thus, **cobaltic aquosulphitotetramminohydroxide,** $[Co(NH_3)_4H_2O(SO_3)]OH.2H_2O$, is formed when cobaltic aquopentamminosulphite or cobaltic aquoenneamminosulphite is treated for two days with a soln. of ammonium thiocyanate. Yellow tetragonal plates of **cobaltic aquosulphitotetrammino-**

thiocyanate, $[Co(NH_3)_4H_2O(SO_3)]CyS.H_2O$, have also been prepared, and when this compound is shaken with silver oxide and water, it is converted into **cobaltic aquosulphitotetramminohydroxide,** $[Co(NH_3)_4H_2O(SO_3)]OH.2H_2O$, which is precipitated by adding alcohol to the filtered liquid. The reddish-yellow, microcrystalline mass is sparingly soluble in water. Hydrochloric acid converts it into the dichlorotetramminochloride ; and with sulphuric acid, it becomes rose-red. A soln. of potassium cyanide converts the hydroxide into the **cobaltic aquosulphitotetramminocyanide,** $[Co(NH_3)_4H_2O(SO_3)]Cy.H_2O$. When cobaltic aquoenneamminosulphite is treated with a soln. of sodium nitrite and ammonium chloride, or acetic acid, it furnishes **cobaltic nitritosulphitotetrammine,** $[Co(NH_3)_4NO_2(SO_3)]$, as a yellow, crystalline powder, which is converted by hydrochloric acid into the praseo-chloride.

There are two series of **disulphitotetrammines,** the *cis* and the *trans*. A. Werner and H. Grüger prepared **ammonium** *cis*-**disulphitotetramminocobaltate,** $NH_4[Co(NH_3)_4(SO_3)_2].3H_2O$, by adding a large excess of ammonium hydrosulphite to the oxidized soln. used in the preparation of the cobaltic sulphitopentammines. It was also made by K. A. Hofmann and A. Jenny, and K. A. Hofmann and S. Reinsch, by the action of sulphur dioxide, or of an ammoniacal soln. of ammonium sulphite, on cobaltic carbonatotetramminochloride. The dark brown, birefringent, monoclinic crystals are freely soluble in warm water, decompose slowly in soln., and when treated with alkalies yield the corresponding alkali salts with evolution of ammonia ; the aq. soln. yields insoluble precipitates with the salts of the alkaline earths, mercury, silver, and gold. It dissolves in conc. sulphuric acid, with evolution of sulphur dioxide, and on adding hydrochloric acid to the soln. the green praseo-salt is precipitated. The salt affords no coloration with ammoniacal sodium nitroprusside, and no precipitate with mercurous nitrate, but slowly gives a flocculent precipitate with thallium nitrate ; in aq. soln. it has half the normal mol. wt. and is regarded as dissociating into the ions NH_4 and $Co(NH_3)_4(SO_3)_2$. The crystals have the axial ratios $a:b:c=0{\cdot}859:1:0{\cdot}534$, and $\beta=111° 23'$; they can give off all their water without decomposition. A. Werner and H. Grüger prepared brownish-yellow leaflets of **ammonium lithium** *cis*-**disulphitotetramminocobaltate,** $2[Co(NH_3)_4(SO_3)_2]Li(NH_4)_2SO_3$, by treating the ammonium salt with lithium hydroxide, in the absence of carbon dioxide ; the salt is soluble in water, but the soln. quickly decomposes. **Ammonium cæsium** *cis*-**disulphitotetramminocobaltate,** $[Co(NH_3)_4(SO_3)_2]Cs.2(NH_4)_2SO_3.2H_2O$, was likewise obtained in dark brown aggregates of crystals. By treating with sodium sulphite the oxidized soln. used in preparing the ammonium salt, **sodium** *cis*-**disulphitotetramminocobaltate,** $Na[Co(NH_3)_4(SO_3)_2].2H_2O$, was obtained in golden-yellow, monoclinic leaflets. The salt was also made by K. A. Hofmann and S. Reinsch, and K. A. Hofmann and A. Jenny. R. Klement prepared **sodium** *cis*-**disulphitodiethylenediaminecobaltate,** $Na[(SO_3)_2Co(C_2H_4(NH_2)_2)_2].3H_2O$. K. A. Hofmann and A. Jenny also prepared rhombic needles of the *trihydrate* by adding alcohol to a dil. soln. of the dihydrate. In aq. soln. the salt has half the normal mol. wt. A. Werner and H. Grüger prepared **potassium** *cis*-**disulphitotetramminocobaltate,** $K[Co(NH_3)_4(SO_3)_2]$, in dark yellow needles ; and **rubidium** *cis*-**disulphitotetramminocobaltate,** $Rb[Co(NH_3)_4(SO_3)_2].2H_2O$, in pale brown needles. They also obtained as precipitates by adding a salt of the metal to a soln. of the ammonium salt, **copper, silver, gold, barium, cadmium, and mercury disulphitotetramminocobaltates.** The corresponding **iron, and nickel disulphitotetramminocobaltates** were very unstable, and could not be isolated. K. A. Hofmann and S. Reinsch, and K. A. Hofmann and A. Jenny prepared **ammonium** *trans*-**disulphitotetramminocobaltate,** $NH_4[Co(NH_3)_4(SO_2)_2].4H_2O$, by crystallization from an aq. soln. of the *cis*-salt. The reddish-yellow prisms are fairly stable in air, but rapidly effloresce in vacuo. Like the cis-salt, it is readily converted into the praseo-chloride, and behaves in a similar manner towards thallium nitrate, mercurous nitrate, and ammoniacal nitroprusside. These two isomeric salts cannot be regarded as merely polymorphous forms of one salt, as they give different colour reactions with sulphuric acid and are not converted into one another by recrystallization. E. H. Riesenfeld and W. Petrich also prepared ammonium *trans*-disulphitotetramminocobaltate, but they regarded it as a dihydrate. They showed that when the *cis*-salt is heated to 150°, it forms **ammonium *trans*-disulphitodiamminocobaltate,** $NH_4[Co(NH_3)_2(SO_3)_2]$. H. Siegert, and R. Klement prepared **sodium disulphitodiamminocobaltate,** $Na[Co(NH_3)_2(SO_3)_2]$. They also prepared **ammonium *trans*-disulphitodiethylenediamminocobaltate,** $NH_4[Co(C_2H_4(NH_2)_2)_2(SO_3)_2]$; and **ammonium *trans*-disulphitodipropylenediaminecobaltate,** $NH_4[Co(C_3H_6(NH_2)_2(SO_3]_2]$; while R. Klement prepared **ammonium *cis*-disulphitoethylenediamine** and the ***trans*-cobaltate,** $NH_4[(SO_3)_2Co(C_2H_4(NH_2)_2)(NH_3)_2].3H_2O$. K. A. Hofmann and A. Jenny prepared **sodium *trans*-disulphitotetramminocobaltate,** $Na[Co(NH_3)_4(SO_3)_2].4H_2O$, in golden-yellow needles, which readily effloresce, and lose all their water in vacuo. K. A. Hofmann and A. Jenny obtained **cobaltic carbonatohydrosulphitotetrammine,** $[Co(NH_3)_4(CO_3)HSO_3]$, by the action of sulphurous acid on the corresponding chloride. It forms violet-red prismatic crystals which yield a violet-red soln. in water; sulphuric acid forms a bluish-red soln., and hydrochloric acid a violet soln. K. A. Hofmann and A. Jenny obtained **aquodisulphitotriamminocobaltic acid,** $H[Co(NH_3)_3(H_2O)(SO_3)_2].H_2O$, as a by-product in the preparation of cobalt hexamminotrisulphite. The dark brown, birefringent, six-sided plates are sparingly soluble in water, and give an amethyst colour with sulphuric acid. By passing sulphur dioxide into an ammoniacal soln. of cobalt acetate which had been exposed for 72 hrs. in air, dark brown rhombic plates of *dihydrated* **sodium aquodisulphitotriamminocobaltate,** $Na[Co(NH_3)_3(H_2O)(SO_3)_2].2H_2O$, were obtained. The salt is sparingly soluble in cold water, and easily soluble in hot water. K. A. Hofmann and S. Reinsch obtained a *trihydrate*, and also a *hexahydrate*.

E. H. Riesenfeld and W. Petrich prepared **ammonium trisulphitotriamminocobaltate,** $(NH_4)_3[Co(NH_3)_3(SO_3)_3]$, by dissolving 10 grms. of cobaltous chloride in 30 c.c. of 7 per cent. aq. ammonia; the greenish-black precipitate was digested with 5 c.c. of 25 per cent. aq. ammonia; the ice-cold filtrate sat. with sulphur dioxide; the filtrate evaporated to half its vol. under reduced press. at 40°–50°; and the filtrate in 3 days furnished reddish-brown prisms. They also prepared yellowish-brown **cobaltic trisulphitotriamminocobaltate,** $Co[Co(NH_3)_3(SO_3)_3]$.

K. A. Hofmann and A. Jenny reported **sodium cobaltic hexamminohexasulphite,** $Na_2Co_3(SO_3)_6.6NH_3.6H_2O$, to be formed by treating an oxidized ammoniacal soln. of cobalt acetate with sulphur dioxide, and adding to the filtrate sodium hydrosulphite, and an excess of ammonia. Yellow plates of the salt appear in about 24 hrs.; and yellow crystals of **sodium cobaltic octamminohexasulphite,** $Na_3Co_3(SO_3)_6.8NH_3.6H_2O$, are formed by passing sulphur dioxide into an ammoniacal soln. of cobalt acetate oxidized by exposure to air, and boiling the precipitate with an ammoniacal soln. of sodium sulphite. K. A. Hofmann and S. Reinsch added cuprous chloride to an ammoniacal soln. of ammonium disulphitotetramminocobaltate, and obtained small, green crystals of **copper cobaltic pentamminotrisulphite,** $CuCo_2(SO_3)_3.5NH_3.H_2O$.

P. Berthier obtained a basic nickel sulphite, as a precipitate, by boiling a soln. of a nickel salt with potassium sulphite. J. S. Muspratt obtained *tetrahydrated* **nickel sulphite,** $NiSO_3.4H_2O$, by passing sulphur dioxide into water with nickelous hydroxide in suspension until almost all has dissolved. The residue appeared as an apple-green, crystalline powder insoluble in water, and soluble in hydrochloric acid with the evolution of sulphur dioxide. He also made it by boiling the soln. obtained by passing sulphur dioxide into water with nickelous carbonate in suspension; and A. Röhrig, by rapidly evaporating a soln. of the hexahydrate at 150°. C. F. Rammelsberg could not prepare the tetrahydrate, but he obtained the *hexahydrate*, $NiSO_3.6H_2O$, in tetrahedral crystals, by evaporating a soln. of nickel hydroxide in sulphurous acid; J. S. Muspratt also obtained this salt; and M. J. Fordos and A. Gélis made it by evaporating a soln. of the metal in sulphurous acid. A. Röhrig showed that the hexahydrate is obtained only from soln. at a temp. below 100°. When the salt is heated, C. F. Rammelsberg showed that the salt melts, water escapes, and the residue solidifies and darkens in colour; sulphur dioxide is then given off and a mixture of nickel oxide and sulphide remains. The salt is insoluble in water, but soluble in sulphurous acid. C. F. Rammelsberg prepared **nickel triamminosulphite,** $NiSO_3.3NH_3.3H_2O$, by treating with alcohol a soln. of nickel sulphite in aq. ammonia. The pale blue crystals decompose when heated giving a sublimate of ammonium sulphite. The salt forms a pale blue soln. with a little water, but the soln. becomes turbid if more water be present, or if the clear soln. be warmed. P. Ray and B. K. Goswami treated a soln. of nickel hydrosulphite with a conc. soln. of hydrazine sulphite and obtained a rose-coloured powder of **nickel trihydrazinosulphite,** $NiSO_3.3N_2H_4.H_2O$, as a granular, insoluble precipitate. It is alkaline towards litmus; and becomes blue when treated with water. It is neither dissolved, nor decomposed by boiling water. It is decomposed explosively by conc. nitric acid. With dil. hydrazine hydrate, a soln. of nickel hydrosulphite forms a pale blue precipitate of **nickel dihydrazinosulphite,** $NiSO_3.2N_2H_4.2H_2O$. The water is not expelled at 150°, and it is decomposed at higher temp. It reacts alkaline towards litmus, and is not decomposed by boiling water. If this salt is suspended in water, and treated with sulphur dioxide and filtered, and the greenish-yellow soln. be evaporated on a water bath, **nickel tetritatrihydrazinosulphite,** $4NiSO_4.3N_2H_4.7H_2O$, is formed. The water is not all expelled at 155°; the salt is neutral towards litmus; it is not dissolved or decomposed by boiling water. K. Seubert and M. Elten obtained **nickel dihydroxydisulphite,** $Ni(OH)_2.2NiSO_3.6H_2O$, by mixing normal soln. of nickel sulphate and sodium sulphite. F. L. Hahn and co-workers prepared **ammonium nickel sulphite** by the method they used for the ammonium copper salt. G. Canneri prepared **thallous nickelous sulphite,** $Tl_2Ni(SO_3)_2$, as a yellow, microcrystalline powder.

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§ 25. The Sulphites of the Platinum Metals

According to J. W. Döbereiner,[1] platinous oxide dissolves freely in sulphurous acid, and the colourless soln., prepared out of contact with air, contains neither sulphates nor sulphides. A. Litton and G. H. E. Schnedermann observed that a soln. of this salt is formed when sulphur dioxide is passed into water with platinous oxide in suspension. J. W. Döbereiner found that on evaporating the soln., a gummy mass is produced which was regarded as a platinic sulphite, but which was shown by L. Gmelin to be more probably **platinous sulphite,** $PtSO_3$. At a red-heat, the colourless salt furnishes sulphuric acid and platinum ; it dissolves easily in water and alcohol ; it is not decomposed by hydrochloric or sulphuric acid ; the aq. soln. becomes brownish-red with stannous chloride, and gives off sulphur dioxide ; the aq. soln. with auric chloride precipitates gold, and forms sulphuric acid and platinum tetrachloride ; and it forms stable, and insoluble colourless complex salts with various sulphites. C. Birnbaum obtained a green, gummy mass of what he regarded as **platinous hydrosulphite,** $Pt(HSO_3)_2$, by treating the alkali platinous salt with potassium fluosilicate, and evaporating the liquid ; he also obtained an unstable soln. of **platinic sulphite,** $Pt(SO_3)_2$, by passing sulphur dioxide into water with platinic oxide in suspension. The dark brown soln. which is produced contains no sulphate ; and if treated with an excess of sulphur dioxide, or allowed to stand out of contact with air, it forms platinous sulphate.

P. T. Cleve prepared a series of what he called *platosamminosulphites*, represented by **platinous** *trans*-**sulphitodiammine,** $[Pt(NH_3)_2SO_3].H_2O$, which he obtained by passing sulphur dioxide through a boiling soln. of platinous nitritodiammine ; evaporating the liquid on water-bath ; adding alcohol ; washing the precipitate with alcohol ; dissolving in water ; evaporating slowly for crystallization ; and drying at 100°. The colourless needles are soluble in water ; and only after treatment with chlorine-water does the soln. give a precipitate with barium chloride. S. G. Hedin reported triclinic plates of complex salts with pyridine, $[PtC_2H_4(NH_2)_2SO_3][Pt(C_5H_5N)_2SO_3].8H_2O$; and $[Pt(C_5H_5N)_2(HSO_3)_2].2\frac{1}{2}H_2O$, the complexes $[Pt(C_6H_5.NH_2)_2(HSO_3)_2]$; $BaSO_3[Pt(C_6H_5NH_2)_2SO_3]$; $BaO.BaSO_3$-$[Pt(C_6H_5NH_2)_2SO_3]$; and $Ag_2SO_3[Pt(C_6H_5NH_2)_2SO_3]$. P. T. Cleve made **platinous** *trans*-**chlorohydrosulphitodiammine,** $[Pt(NH_3)_2(HSO_3)Cl]$, in white needles, by evaporating a soln. of platinous dichlorodiammine sat. with sulphur dioxide ; M. Peyrone, and P. T. Cleve, **platinous** *trans*-**chlorammoniosulphitodiammine,** $[Pt(NH_3)_2(NH_4SO_3)Cl].H_2O$, in colourless rhombic plates, by boiling a soln. of platinous dichlorodiammine with an excess of ammonium sulphite. M. Peyrone obtained **ammonium platinous** *trans*-**sulphitodiamminosulphite,** $(NH_4)_2SO_3[Pt(NH_3)_2SO_3]$, by the action of an excess of ammonium sulphite on platinous *trans*-dichlorodiammine ; and P. T. Cleve, by adding alcohol to a soln. of platinous *trans*-dichlorodiammine and ammonium sulphite. The colourless, rhombic scales are soluble in water, and when oxidized with aqua regia furnish yellow octahedra of platinic *trans*-tetrachlorodiammine. W. Haberland and G. Hanekop obtained **sodium platinous** *trans*-**sulphitodiamminosulphite,** $Na_2SO_3[Pt(NH_3)_2SO_3].5\frac{1}{2}H_2O$, by saturating a soln. of hydrochloroplatinic acid with sulphur dioxide ; neutralizing the liquid with sodium carbonate ; dissolving the white precipitate in hydrochloric acid ; and adding an excess of ammonia to the acidic liquid. The colourless, rhombic crystals have, according to S. L. Tornquist, the axial ratios $a : b : c = 0·8731 : 1 : 1·4456$; and have a negative double refraction. W. Haberland and G. Hanekop said that when heated to 100°, $3\frac{1}{2}$ mols. of water are expelled along with some ammonia and sulphur dioxide ; at 135°, 5 mols. of water are expelled and the salt decomposes ; and at a higher temp., it leaves a residue of sodium sulphate and platinum. 100 c.c. of water at 20° dissolve 5·37 grms. of salt. Sulphuric acid decomposes the salt giving off sulphur dioxide; and boiling potash-lye develops ammonia. P. T. Cleve prepared **cupric platinous** *trans*-**sulphitodiamminosulphite,** $CuSO_3[Pt(NH_3)_2SO_3].5H_2O$, in bluish-green crystals, sparingly soluble in water; **silver platinous** *trans*-**sulphitodiamminosulphite,** $Ag_2SO_3[Pt(NH_3)_2SO_3].H_2O$, as a snow-white powder; **barium platinous** *trans*-**sulphitodiamminosulphite,** $BaSO_3[Pt(NH_3)_2SO_3].3H_2O$, in colourless needles; **zinc platinous** *trans*-**sulphitodiamminosulphite,** $ZnSO_3$-$[Pt(NH_3)_2SO_3].6H_2O$, in small plates or prisms; **lead platinous** *trans*-**sulphitodiamminosulphite,** $PbSO_3[Pt(NH_3)_2SO_3].H_2O$, as a white crystalline powder; **uranyl platinous** *trans*-**sulphitodiamminosulphite,** $UO_2SO_3[Pt(NH_3)_2SO_3].H_2O$, as a yellow crystalline powder which becomes anhydrous at 100°; **manganous platinous** *trans*-**sulphitodiamminosulphite,** $MnSO_3[Pt(NH_3)_2SO_3].4H_2O$, as a white powder consisting of prismatic crystals; **cobaltous platinous** *trans*-**sulphitodiamminosulphite,** $CoSO_3[Pt(NH_3)_2SO_3].6H_2O$, in rose-coloured crystals; and **nickel platinous** *trans*-**sulphitodiamminosulphite,** $NiSO_3[Pt(NH_3)_2SO_3].7H_2O$, in bluish or greenish microscopic plates.

P. T. Cleve prepared **ammonium platinous** *cis*-**sulphitodiamminosulphite,** $2(NH_4)_2SO_3[Pt(NH_3)_2SO_3]$, by adding alcohol to a soln. of *cis*-dichlorodiammine containing an excess of ammonium sulphite. The colourless, four-sided needles are soluble in water. **Sodium platinous** *cis*-**sulphitodiamminosulphite,** Na_2SO_3-$[Pt(NH_3)_2SO_3].4H_2O$, was prepared as in the case of the *trans*-salt. Similarly with **silver platinous** *cis*-**sulphitodiamminosulphite,** $2Ag_2SO_3[Pt(NH_3)_2SO_3]$; **barium platinous** *cis*-**sulphitodiamminosulphite,** $2BaSO_3[Pt(NH_3)_2SO_3]$; and colourless prisms or plates of **platinous** *cis*-**chlorohydrosulphatodiammine,** $[Pt(NH_3)_2(HSO_3)Cl]$, by the action of sulphur dioxide on a soln. of the *cis*-dichloro- or tetrachlorodiammine; M. Peyrone, white needles of **ammonium platinous** *cis*-**chloroamminosulphitodiamminosulphite,** $(NH_4)_2SO_3[Pt(NH_3)_2(NH_4SO_3)Cl].\frac{1}{2}H_2O$, by boiling a soln. of ammonium sulphite with an excess of the *cis*-dichlorodiammine; and P. T. Cleve, **ammonium platinous** *cis*-**ammoniumchlorosulphitodiamminosulphite,** $(NH_4)_2SO_3[Pt(NH_3)_2SO_3][Pt(NH_3)_2(NH_4SO_3)Cl].2H_2O$, in colourless needles easily soluble in water, by boiling a mixed soln. of ammonium platinous *cis*-sulphitodiamminosulphite with an excess of platinous *cis*-dichlorodiammine, and adding alcohol to the filtrate from the cold soln.

C. Birnbaum prepared **platinous tetramminosulphite,** $[Pt(NH_3)_4]SO_3$, by warming a dil. soln. of ammonium platinous trichlorohydrosulphite, with ammonia: $2NH_4Cl.Pt(HSO_3)Cl+5NH_3=3NH_4Cl+[Pt(NH_3)_4]SO_3$. The white precipitate forms long needles on standing in water; but D. Strömholm said that what appears to be the same compound was obtained as **platinous triamminosulphite,** $PtSO_3(NH_3)_3$, by the action of ammonia on a warm soln. of ammonium trichlorosulphonate. When its hydrochloric acid soln. is oxidized with chromic acid, platinous *trans*-diamminodichloride, $Pt(NH_3)_2Cl_2$, is formed. P. T. Cleve made **platinous tetramminobishydrosulphite,** $[Pt(NH_3)_4](HSO_3)_2.2H_2O$, in colourless octahedra or prisms, by mixing soln. of platinic dichlorotetramminodinitrate with sulphurous acid; but D. Strömholm said that the compound is really **platinic tetramminodisulphite,** $Pt(NH_3)_4(SO_2)_2.2H_2O$. When oxidized by chromic acid, the oxygen is consumed chiefly in oxidizing the sulphite to sulphate. When boiled with water, or heated with acids, platinous tetramminosulphate is formed, the quadrivalent platinum being reduced by half the sulphurous acid, which becomes oxidized to sulphuric acid, whilst the other half of the sulphurous acid escapes. The same reaction takes place incompletely when the salt is heated. P. T. Cleve, and M. Peyrone made *dihydrated* **platinous tetramminodisulphite,** $3[Pt(NH_3)_4]SO_3.$ $PtSO_3.2H_2O$, in thin needles, by mixing platinous tetramminodichloride with a hot, conc. soln. of sodium hydrosulphite. By working with a cold soln., M. Peyrone made the *tetrahydrate;* and O. Carlgren and P. T. Cleve obtained it, in four-sided prisms, by the action of hot sulphurous acid on the complex iodoamminonitrate.

P. T. Cleve, and M. Peyrone also prepared **platinous tetramminodihydrotrisulphite,** $2[Pt(NH_3)_4](HSO_3)_2.PtSO_3$, by the action of ammonium sulphite on platinous tetramminoplatinic chloride.

J. von Liebig obtained **ammonium platinous disulphite,** $(NH_4)_2SO_3.PtSO_3.H_2O$, by adding alcohol to a soln. of hydrochloroplatinic acid neutralized with ammonia, and saturating with sulphur dioxide; washing the precipitate with alcohol; and drying over sulphuric acid. The white crystals were found by C. Birnbaum to lose water at 110°. The crystals form a colourless soln. with water. The soln. gives a white precipitate with silver nitrate, and no precipitate with potash-lye, or alkali hydroxide unless mixed with hydrochloric acid. The diammines are described above. P. T. Cleve prepared **ammonium platinous tetrasulphite,** $3(NH_4)_2SO_3.PtSO_3$, by evaporating a mixed soln. of platinous chloride and ammonium sulphite in the presence of aniline; and by J. Lang, by treating ammonium chloroplatinite with ammonium sulphite, washing the precipitate with cold water. The colourless needles are slightly soluble in cold water, and more soluble in hot water; when treated with sodium carbonate, ammonia is evolved. C. Birnbaum prepared the *trihydrate,* $3(NH_4)_2SO_3.PtSO_3.3H_2O$, by the action of sulphur dioxide on a soln. of ammonium sulphite in which hydrated platinic oxide is suspended, neutralizing the soln. with ammonia, evaporating, and drying over sulphuric acid.

A. Litton and G. H. E. Schnedermann, and C. Birnbaum prepared **sodium platinous disulphite,** $Na_2SO_3.PtSO_3.H_2O$, by evaporating a soln. of the tetrasulphite in dil. sulphuric or hydrochloric acid, washing the product with a little water, and drying at 100°. The yellow powder is sparingly soluble in water, and the soln. gives no precipitate with sodium chloride. A. Litton and G. H. E. Schnedermann treated platinous sulphite, and J. Lang, and C. Birnbaum, potassium sulphitoplatinite, with sodium carbonate, and dried the product over sulphuric acid. A. Litton and G. H. E. Schnedermann added sodium carbonate to a soln. of hydrochloroplatinic acid, sat. with sulphur dioxide, and dried at 200° the washed precipitate; P. T. Cleve boiled soln. of platinous dichlorodiammine with sodium sulphite; E. von Meyer saturated a soln. of platinum dichlorofulminate with sulphur dioxide, neutralized it with sodium carbonate, and dried the product at 100°; and C. Rudelius treated *trans*-platinous dichlorodisulphopropylamine with sodium sulphite. The white powder has a yellow tinge, and consists of minute needles; C. Birnbaum represented the salt as a heptahydrate; J. Lang, P. T. Cleve, E. von Meyer, and C. Rudelius, as a hemitrihydrate; and S. Tyden regarded the product he obtained from sodium sulphite and sodium platinous dithiodiglycollate as a dihydrate. C. Birnbaum's heptahydrate lost 5½ mols. of water at 100°, and at 180° all the water is given off. J. Lang found that decomposition starts at about 240°. The salt was found by A. Litton and G. H. E. Schnedermann to be sparingly soluble in cold water; more soluble in hot water; insoluble in a soln. of sodium chloride, and in alcohol. The aq. soln. is decomposed by chlorine; acids dissolve the salt with the evolution of sulphur dioxide; hydrogen sulphide, and ammonium sulphide give no precipitate with the aq. soln. until an acid has been added, when platinic sulphide is precipitated; sodium, ammonium, and barium chlorides give a white precipitate, so also does silver nitrate; ammonia precipitates a tetrammine from the soln. in hydrochloric acid; sulphuric acid forms sodium and platinous sulphates; potassium cyanide forms a cyanoplatinite; and boiling alkali-lye does not decompose a soln. of the salt.

J. Lang prepared **potassium platinous tetrasulphite,** $3K_2SO_3.PtSO_3.1\frac{1}{2}H_2O$, in colourless or pale yellow, six-sided prisms, by cooling a hot soln. of potassium chloroplatinite and potassium hydrosulphite. The salt is dried in vacuo or over sulphuric acid; it is sparingly soluble in cold water, and freely soluble in hot water; the soln. has a neutral reaction; ammonia gives a white precipitate which disappears on shaking; potassium hydroxide or carbonate gives no precipitate; sodium carbonate precipitates the sodium salt; dil. soln. of ammonium carbonate, and hydrogen sulphide give no precipitate; ammonium sulphide with a boiling soln., and after the addition of hydrochloric acid, gives a black precipitate; hydrochloric acid very slowly decomposes the warm soln., giving off sulphur dioxide; and mercurous nitrate gives a yellowish-green precipitate. C. Birnbaum obtained the *dihydrate*, which is probably the same as the alleged hemitrihydrate, from the soln. obtained by passing sulphur dioxide into an aq. soln. of potassium sulphite in which hydrated platinic oxide is suspended. The liquid is neutralized with potassium carbonate and evaporated; the crystals are dried over sulphuric acid. S. Tyden obtained a *tetrahydrate*, $K_6Pt(SO_3)_4.4H_2O$, by the action of potassium carbonate and pyrosulphite on platinous dithioglycollate. C. Claus obtained **potassium platinous decasulphite,** $6K_2O.2PtO.10SO_2.5H_2O$, from a boiling soln. of potassium chloroplatinate and potassium sulphite; but J. Lang could not verify this result. For copper platinous diamminosulphite, *vide supra*, the diammines. J. Lang prepared silver platinous tetrasulphite, $3Ag_2SO_3.PtSO_3$, by treating the potassium salt with silver nitrate. The white salt blackens in light, and is soluble in aq. ammonia—for the diammines, *vide supra*.

C. Birnbaum obtained **ammonium platinous dichlorodisulphite,** $(NH_4)_4PtCl_2(SO_3)_2$, in colourless prisms, from the action of a soln. of ammonium hydrosulphite on ammonium chloroplatinite or ammonium platinous trichlorohydrosulphite; C. Birnbaum, and P. Schottländer, **ammonium platinous trichlorohydrosulphite,** $2NH_4Cl.Pt(HSO_3)Cl$, in orange-yellow needles, from a soln. of ammonium chloroplatinite in warm conc. sulphurous acid; and C. Birnbaum, **ammonium platinous chlorodisulphite,** $(NH_4)_2SO_3.(NH_4)Pt(SO_3)Cl.3H_2O$, in pale yellow monoclinic crystals, from a soln. of ammonium chloroplatinite in a conc. soln. of ammonium sulphite. The ammines of the chlorosulphites have been already discussed. E. A. Hadow reported **platinous diammins pentachlorosulphite,** $2[Pt(NH_3)_2Cl_2]PtSO_3.PtCl_2$. C. Birnbaum made **potassium platinous trichlorosulphite,** $2KCl.KPt(SO_3)Cl$, in orange-yellow crystals, from a soln. of potassium chloroplatinate in warm, conc. sulphurous acid; **ammonium potassium platinous chlorodisulphite,** $(NH_4)KSO_3.KPt(SO_3)Cl.3H_2O$, in colourless prisms, from a warm soln. of ammonium chloroplatinite, ammonium hydrosulphite, neutralized with potassium carbonate; and **ammonium potassium platinous trichlorosulphite,** $2NH_4Cl.KPt(SO_3)Cl$. in orange-yellow, rhombic crystals, from a soln. of potassium carbonate and ammonium platinous trichlorohydrosulphite. The platinous chlorosulphites can be represented as members of the series:

$$K_2[PtCl_4] \qquad K_3[PtCl_3(SO_3)] \qquad (NH_4)_4[PtCl_2(SO_3)_2] \qquad K_6[Pt(SO_3)_4]$$

C. Birnbaum made **potassium platinic oxydisulphite,** $K_2SO_3.PtO(SO_3).H_2O$, by passing sulphur dioxide into water with hydrated platinic oxide in suspension until the brown powder begins to dissolve, and the remainder then slowly dissolves. The filtrate was mixed with potassium sulphite, and potassium carbonate added until the liquid has a feeble acidic reaction; washed with cold water; and dried over sulphuric acid. The dark brown powder consists of minute crystals. It loses water at 100°, and decomposes at 120°. Hydrogen sulphide reduces the soln. to a colourless platinous salt, and with acidic soln. hydrogen sulphide and ammonium sulphide precipitate platinic sulphide; hydrochloric acid displaces the sulphur dioxide; potash-lye forms a brown soln., and on boiling no hydrated platinic oxide is separated; and barium chloride gives a yellow precipitate. C. Birnbaum obtained **sodium platinic oxydisulphite,** $Na_2SO_3.PtO(SO_3).2H_2O$, in an analogous way.

C. Claus, and K. Seubert could not isolate **iridous sulphite,** $IrSO_3$, but they obtained complex salts with the alkaline sulphites, some of which have been regarded as salts of an unknown **hydrosulphitoiridous acid,** $H_2Ir(SO_3)_2$, or **iridous hydrosulphite,** $Ir(HSO_3)_2$. C. Claus found that when iridous chloride is mixed with potassium hydrosulphite, a yellow precipitate is formed with the composition $3K_2O.IrO.5SO_2$, which was thought to be a mixture containing *potassium iridous sulphite.*

According to C. Birnbaum, if hydrated iridium dioxide be suspended in water, and treated with a current of sulphur dioxide, part of the iridium oxide is reduced and passes into soln. as a sulphite, and the green soln. deposits yellow crystals of iridium trisulphite, $Ir_2(SO_3)_3.6H_2O$. This salt is washed with water and dried over sulphuric acid. It loses all its water at 160°–180°; and when heated to a higher temp., it gives off water, and sulphur dioxide; and finally sulphuric acid, leaving a residue of the black hemitrioxide. The salt is sparingly soluble in water, and freely soluble in acids with the evolution of sulphur dioxide. Alkali-lye converts the sulphite into the hemitrioxide which in air oxidizes to the dioxide. In the preparation of the normal sulphite the part which does not dissolve in sulphurous acid is a dirty olive-green *iridium oxysulphite*, or *iridyl sulphite*, $IrO(SO_3).4H_2O$, with quadrivalent iridium; or it may be a basic sulphate, $Ir_2O(SO_4)_2.8H_2O$. C. Birnbaum obtained **ammonium iridium trisulphite,** $(NH_4)_3Ir(SO_3)_3.1\frac{1}{2}H_2O$, by adding ammonium carbonate to a soln. of iridium trisulphite. The brown crystalline powder is insoluble in water; the corresponding **potassium iridium trisulphite,** $K_3Ir(SO_3)_3.3H_2O$; and **sodium iridium trisulphite,** $Na_3Ir(SO_3)_3.4H_2O$, were produced in a similar way. If the sodium salt be dissolved in hot hydrochloric acid, and the red soln. be saturated with ammonia, it deposits a yellow precipitate, which, when crystallized from its aq. soln., furnishes **sodium iridium enneamminohexasulphite,** $Na_3Ir_2(NH_3)_9(SO_3)_6.10H_2O$.

K. Seubert observed that when a soln. of ammonium chloroiridite or chloroiridate is treated with sulphur dioxide at about 70°, the liquid acquires a red colour, and deposits orange crystals of **ammonium iridium hexachlorodihydrosulphite,** $4NH_4Cl.IrCl_2.H_2SO_3$, which are very soluble in water. C. Claus[2] obtained **potassium iridium chlorotrisulphite,** $2K_2SO_3.IrCl(SO_3)$, as a yellow powder decomposed by boiling water; and hexagonal crystals of **potassium iridium tetrachlorodisulphite,** $2KCl.2K_2SO_3.IrCl_2.12H_2O$, from a hot mixture of potassium hydrosulphite and chloroiridite; a soln. of this salt in hydrochloric acid yields, on evaporation, **potassium iridium pentachlorodisulphite,** $3KCl.K_2SO_3.IrCl_2(SO_3).2H_2O$.

J. J. Berzelius found that when a soln. of osmium tetroxide is reduced with sulphur dioxide, the yellow liquid becomes indigo-blue, and when evaporated out of contact with air, and dried at 100°, in vacuo, **osmious sulphite,** $OsSO_3$, is formed as a black powder. C. Claus and E. Jacoby obtained it from a soln. of osmium oxysulphide in conc. sulphurous acid; and E. Frémy, by treating potassium osmiate with the same acid. The powder is insoluble in water, but soluble in acids. When heated, it decomposes $2OsSO_3=OsS+OsO_4+SO_2$; with alkali-lye, it forms osmious hydroxide and alkali sulphite. C. Claus treated potassium chlorosmiate with potassium sulphite and obtained the complex salt $2K_2SO_3.2KHSO_3.4H_2O$, **potassium osmious dihydrotetrasulphite.** The tabular crystals are almost tasteless; they decompose at 180°; are insoluble in water; and react like the iridium salt. A soln. of this salt in hydrochloric acid furnishes reddish-brown, soluble crystals of **potassium osmium disulphite,** $6KCl.OsO.2SO_2$.

According to A. Rosenheim and E. A. Sasserath, if sulphur dioxide be passed into a soln. of osmium tetroxide in 20 per cent. sodium hydroxide, until the soln. is nearly neutral to litmus, and the soln. neutralized with sodium hydrosulphite, **sodium osmictetrasulphite,** $3Na_2O.OsO_3.4SO_2.5H_2O$, or, neglecting the water of crystallization, $(NaO)_2Os(NaSO_3)_4$, is formed. This salt is also obtained by cautiously adding sodium hydrosulphite to a soln. of sodium osmate. The salt furnishes reddish-brown needles; it forms a reddish-brown soln. with water at 70°, and this soon decomposes with the precipitation of the black oxide; with sodium hydroxide it forms a violet soln. of sodium osmiate, with silver nitrate, reddish-brown **silver osmic sulphide;** and with barium chloride, brown **barium osmic sulphide.** If a 20 per cent. soln. of potassium hydroxide be substituted for sodium hydroxide, **potassium osmic decasulphite,** $7K_2O.4OsO_3.10SO_2.7H_2O$, or $(KO)_2Os_2(OH)_5(KSO_3)_4.H_2O$, is formed. It is more soluble than the sodium salt, and it decomposes at 70°. It furnishes a trihydrate and the anhydrous salt. By using a more conc. soln. of potash-lye, **potassium osmic tetradecasulphite,** $11K_2O.4OsO_3.14SO_2.H_2O$, or $(KO)_2Os_2(OH)_5(KSO_3)_5.2K_2SO_3$, is formed. It is supposed that the potassium salt is derived from an osmate, $(KO)_2Os_2O_5$, as just indicated. No ammonium osmic sulphite could be prepared.

G. Sailer prepared dark violet **sodium osmium sulphite,** $Na_6[Os_4(SO_3)_7].24H_2O$, by the action of sodium hydrosulphite on an alkaline soln. of osmium chloride. A. Rosenheim and E. A. Sasserath prepared **sodium hexasulphitosmate,** $Na_8[Os(SO_3)_6].8H_2O$, by boiling an aq. soln. of sodium chlorosmate with a conc. soln. of sodium hydrosulphite. It crystallizes from dil. sodium hydrosulphite in microscopic, brownish-white prisms, is sparingly soluble in water, and decomposes with a bluish-green coloration, gives an intense blue precipitate when treated with alkali, and does not yield all its sulphurous acid when boiled with conc. hydrochloric acid. It is also obtained with 3 mols. of water of crystallization by leaving a mixed soln. of sodium chlorosmate and hydrosulphite in a closed flask for some weeks. By boiling the mixed soln., **sodium aquopentasulphitosmate,** $Na_6[Os(H_2O)(SO_3)_5].4H_2O$, is obtained as a white crystalline powder; and by heating a mixed soln. of sodium chlorosmate and sulphite at 70°, **sodium chloropentasulphitosmate,** $Na_7OsCl(SO_3)_5].6H_2O$, is obtained as a white crystalline powder; and by heating a mixed soln. of sodium chlorosmate and sulphite at 70°; the salt is a violet crystalline powder, which dissolves in boiling water with a reddish-violet coloration and then decomposes, yielding a violet precipitate. The chlorine in this compound cannot be precipitated quantitatively with silver nitrate. If an excess of sodium hydrosulphite or sulphite acts, for a long time, on sodium chloro-osmate at ordinary temp., A. Rosenheim obtained **sodium dichlorotetrasulphitosmate,** $Na_6[OsCl_2(SO_3)_4].10H_2O$; while A. Rosenheim and E. A. Sasserath found that when the two soln. react at 50°, **sodium oxytetrasulphitosmate,** $Na_6[OsO(SO_3)_4].3H_2O$, is formed as a violet, crystalline precipitate. When a soln. of potassium osmic sulphite and hydrosulphite is boiled, **potassium dihydrohexasulphitosmate,** $K_2H_2[Os(SO_3)_6].2H_2O$, crystallizes out in white needles. It is more easily soluble than the sodium salt, and can be recrystallized from water without decomposition. It is also obtained by boiling potassium tetrachlorosmate with potassium hydrosulphite and by allowing a mixture of potassium osmic sulphite and potassium hydrosulphite to remain at the ordinary temp. If potassium sulphite be added to a cold soln. of potassium chlorosmate, white needles of **potassium aquopentasulphitosmate,** $K_6[Os(H_2O)(SO_3)_5].4H_2O$, are formed along with a small proportion of yellow acicular crystals of a chloro-salt. White or pale rose-coloured **potassium trihydroaquohenasulphitosmate,** $K_{11}H_3[Os(H_2O(SO_3)_{11}].5H_2O$, is formed by the action of soln. of potassium hydrosulphite and potassium osmic sulphite in the cold or gently warmed. This salt can be recrystallized from water without decomposition. A. Rosenheim prepared **potassium dihydrotetrachlorotetrasulphite,** $K_6H_2[OsCl_4(SO_3)_4]$, by the prolonged action of soln. of potassium hydrosulphite and chlorosmate. The dark red, monoclinic crystals have the axial ratios $a:b:c=1{\cdot}7243:1:1{\cdot}1729$, and $\beta=105°\ 44'$. When heated with hydrochloric acid, sulphur dioxide is evolved, and potassium chlorosmate is formed.

F. Frerichs and F. Wöhler[3] prepared **sodium palladous tetrasulphite,** $2Na_2SO_3.Na_2Pd(SO_3)_2.2H_2O$, by saturating a soln. of palladous chloride with sulphur dioxide, and adding sufficient sodium hydroxide to neutralize the liquid, a white crystalline precipitate is formed, which when washed and dried is pale yellow. The salt dissolves in boiling water, but does not separate out on cooling; it is also soluble in soda-lye, and in sulphurous acid.

C. Claus[4] prepared **rhodium trisulphite,** $Rh_2(SO_3)_3.6H_2O$, by dissolving the hydrated oxide in sulphurous acid; evaporating the soln.; and washing out the excess of acid with alcohol. The white crystals are soluble in water, but not in alcohol. When heated, sulphur dioxide and sulphuric acid are given off, and rhodium hemitrioxide remains. J. J. Berzelius, E. Frémy, and C. Claus mixed sulphurous acid, or potassium hydrosulphite, with a soln. of potassium rhodium chloride, and obtained a white precipitate of **potassium rhodium trisulphite,** $3K_2SO_3.Rh_2(SO_3)_3.6H_2O$, or $K_3Rh(SO_3)_3.3H_2O$. The sulphite is insoluble in water; is attacked slowly by acids; at a red-heat forms potassium sulphate and rhodium; when boiled with hydrochloric acid, sulphur dioxide is given off, and the corresponding chloride is formed; and boiling potash-lye does not decompose the salt. R. Bunsen made **sodium rhodium sulphite** in a similar way; and K. Seubert and K. Kobbé assigned to it the formula $6Na_2SO_3.4RhSO_3.9H_2O$. The green product is insoluble in cold water, and sparingly soluble in hot water; and a kind of anhydrous alum is formed with sulphuric acid. G. Sailer reported **brownish-red sodium rhodium sulphite,** $Na_6[Rh_4(SO_3)_7].12H_2O$, to be formed by the action of sodium hydrosulphite on an alkaline soln. of rhodium chloride.

According to U. Antony and A. Lucchesi,[5] when a soln. of ruthenium sulphate is treated with sulphur dioxide, the colour of the soln. changes from bright red, through green and violet, to azure-blue, after which the liquid is decolorized. If the azure-blue soln. is poured into alcohol, there is formed a precipitate of **ruthenium trisulphite,** $Ru_2(SO_3)_3.nH_2O$. The blue compound is an intermediate stage in the conversion of the sulphate to dithionate. It is a blue colloid, and dissolves in a large quantity of water, giving a soln. from which it is completely precipitated by the addition of a salt. It can be dried at 80° without change, but when heated in a current of carbon dioxide or nitrogen, it begins to lose sulphur dioxide at 100°, and on stronger heating is completely decomposed, with the formation of a brown substance. C. Claus showed that when sulphur dioxide acts on a soln. of potassium ruthenium chloride at ordinary temp., a yellow powder of **potassium ruthenous disulphite,** $K_2Ru(SO_3)_2$, is formed; a similar product is obtained when the double salt is heated with potassium hydrosulphite. According to A. Miolati and C. C. Tagiuri, when potassium ruthenium pentachloride is boiled with a soln. of potassium hydrosulphite, a blue, crystalline precipitate of **potassium ruthenium oxyoctosulphite,** $O[Ru(SO_3)_4K_6]_2.4H_2O$, is formed; and similarly with **sodium ruthenium oxyoctosulphite,** $O[Ru(SO_3)_4K_6]_2.2H_2O$. By the action of sodium hydrosulphite on ruthenium chloride in alkaline soln., G. Sailer obtained brownish-yellow **sodium ruthenium hydrosulphite,** $Na_3H_3[Ru(SO_3)_4]$. A. Miolati and C. C. Tagiuri found that if a soln. of hydrosulphite acts on sodium nitrosochlororuthenate, small orange-yellow crystals of **sodium oxynitrosotetrasulphite,** $O[Ru(SO_3)_2(NO)Na_2]_2.2H_2O$, are formed. They are slightly soluble in cold water. Needle-like crystals of **potassium oxynitrosotetrasulphite,** $O[Ru(SO_3)_2(NO)K_2].2H_2O$, are formed in a similar way.

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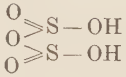
§ 26. Pyrosulphurous Acid and the Pyrosulphites

The hypothetical **pyrosulphurous acid,** $H_2S_2O_5$,



$$\begin{array}{l} O \\ \quad \geqslant S-OH \\ O \\ \quad \geqslant S-OH \\ O \end{array}$$

has not been prepared, although a few of its salts—**pyrosulphites**—have been prepared by J. S. Muspratt,[1] E. Carey and F. Hurter, C. Schultz-Sellack, A. Röhrig, M. Berthelot, A. Bernthsen and M. Bazlen, F. Basse and G. Faure, A. Geuther, etc. W. Meysztowicz could not prepare pyrosulphites of the bivalent metals. When treated with acids, the pyrosulphites furnish sulphurous acid ; and when heated, A. H. Röhrig, and M. Berthelot represented the decomposition $2R_2S_2O_5=2R_2SO_4+S+SO_2$; A. Geuther said that some thiosulphate is formed as an intermediate product, but E. Divers did not agree with this. P. G. Hartog supposed that the molecule should be doubled $R_4S_4O_{10}$ because of the evolution of heat at these stages during the progressive neutralization of sulphurous acid and ammonia. M. Berthelot also believed that the molecule of the metasulphite should be doubled. R. Dietzel and S. Galanos said that aq. and alcoholic soln. of ammonium and potassium pyrosulphites show no spectrum characteristic of S_2O_5''-ions ; and the state of equilibrium in these cases is similar to that with aq. soln. of sulphur dioxide (*q.v.*).

A. F. de Fourcroy and L. N. Vauquelin mentioned the formation of an acid ammonium sulphite as a sublimate when the normal sulphite is heated. J. C. G. de Marignac obtained **ammonium pyrosulphite,** $(NH_4)_2S_2O_5$, by saturating a soln. of the normal with sulphur dioxide, and R. de Forcrand, by saturating conc. aq. ammonia with that gas, and evaporating the soln. in vacuo over sulphuric acid ; A. Fock and K. Klüss, and E. Divers and M. Ogawa employed a similar mode of preparation. E. Divers and M. Ogawa said that if, in the preparation of the salt, the passage of sulphur dioxide is not stopped when the soln. is full of crystals, these gradually dissolve, and the soln. becomes greenish-yellow. Then, as it becomes sat. with sulphur dioxide in the cooling mixture, the pyrosulphite crystallizes out—a quantity equivalent to a little more than one-fifth of the ammonia taken is thrown out of soln. by the sulphur dioxide. The salt can be obtained dry and pure in the same way as the normal sulphite, except that sulphuric acid, to which a little solid alkali sulphite has been added, is used in the desiccator. It may be kept unchanged for any time in such a desiccator, although it is very deliquescent and changeable when not carefully preserved from moisture. This salt is also easily obtainable by evaporating its aq. soln., but not without some decomposition through loss of sulphur dioxide and through oxidation with formation of sulphate. J. S. Muspratt made the salt by passing the two moist gases into ether. The preparation of the sulphite as a by-product in other preparations was discussed by G. Blattner, and by E. Carey and F. Hurter. The pyrosulphite furnishes rhombic crystals, which, according to J. C. G. de Marignac, and A. Fock and K. Klüss, have the axial ratios $a : b : c=0{\cdot}3939 : 1 : 0{\cdot}4770$. They are not isomorphous with the potassium salt. The crystals are difficult to measure on account of their tendency to deliquesce :

R. de Forcrand gave for the heat of formation $(2S_{solid},5O_{gas},4H_{2gas},N_{2gas})$ =300·00 Cals.; $(2S_{gas},5O_{gas},4H_{2gas},N_{2gas})$=305·20 Cals.; $((NH_4)_2S_2+5O)$=234·0 Cals.; $(2SO_{2gas},2NH_{3gas},2H_2O_{gas})$=80·00 Cals.; for aq. soln., $2SO_2$(64 grms. in 4 litres) and $(NH_4)_2O$(26 grms. in 2 litres), 59·12 Cals., and $2SO_2$(64 grms. in 2 litres) and $2(NH_4)_2O$(26 grms. in 2 litres), 25·00 Cals. For the reaction of a mol of the pyrosulphite in 12 litres of water, and a mol of $(NH_4)_2O$ in 2 litres, 20·74 Cals. The heat of soln. of one mol of salt in 60 parts of water, is −6·38 Cals. at 8°. According to E. Divers and M. Ogawa, the thoroughly dry pyrosulphite sublimes unchanged at 130°–150°, but probably with an intermediate dissociation; and if any moisture be present, some sulphate and trithionate are formed. G. A. Barbaglia and P. Gucci found that the pyrosulphite in a sealed tube at about 150° furnishes ammonium sulphate, sulphuric acid, and sulphur. A. Bineau found that the salt can be heated to 134° without giving off gas, and that mercury is blackened. All agree that the pyrosulphite is extremely deliquescent, and is difficult to dry without oxidation; J. C. G. de Marignac found that the crystals lose sulphur dioxide on exposure to air; and J. S. Muspratt, that half the combined sulphur dioxide is given off in air, and that the salt is readily oxidized to the normal sulphate. F. Rochleder found that the conc. aq. soln., in darkness, suffers no change in air; but in diffused light, and in air, sulphur is deposited and ammonium sulphate with a little thiosulphate are formed. J. S. Stas said that the pyrosulphite changes its titre in light. The action of the salt on ammonium iodide and iodic acid resembles that of the normal sulphate; the reduction to hyposulphite by zinc was observed by M. Prud'homme; and the electrolysis of the ammoniacal soln., by G. Halphen. W. Eidmann found that it is insoluble in acetone. A. P. Sabanéeff and W. Speransky obtained hydrazine pyrosulphate, $(N_2H_4)_2H_2S_2O_7$, by passing sulphur dioxide into an aq. soln. of hydrazine hydrate, and evaporating the yellow soln. under reduced press., or in an atm. of sulphur dioxide; or else precipitating the salt from the soln. with alcohol. The salt readily oxidizes to the sulphate. The effect of the salt on the f.p. of water corresponds with the factor i=3·82 to 3·55 with respectively a conc. of 1·152 and 4·548 grms. per 100 grms. of water.

A. P. Sabanéeff[2] prepared **hydrazine pyrosulphite,** $2N_2H_4.H_2S_2O_5$, *i.e.* $(N_2H_5)_2S_2O_5$, by passing sulphur dioxide into an aq. soln. of hydrazine hydrate—*vide supra*, hydrazine sulphite.

When sulphur dioxide in excess is passed into a conc. aq. soln. of sodium carbonate, crystals of **sodium pyrosulphite,** $Na_2S_2O_5$, are deposited as the soln. cools—*vide supra*. An analogous process was used by C. Schultz-Sellack,[3] E. J. Maumené, A. F. de Fourcroy and L. N. Vauquelin, A. H. Röhrig, and R. E. Evans and C. H. Desch; H. Endemann treated a cold, dil., aq. soln. similarly; E. Carey and F. Hurter treated solid monohydrated sodium carbonate with the gas; and F. Basse and G. Faure devised a continuous process for preparing this salt by the action of sulphur dioxide on a soln. of sodium carbonate. Both A. Röhrig and C. F. Rammelsberg obtained a *hemihydrate*, $Na_2S_2O_5.\frac{1}{2}H_2O$, by evaporating the soln. at room temp. or from a warm acid soln. Otherwise the analyses of H. Endemann, A. Röhrig, and R. E. Evans and C. H. Desch agree with $Na_2S_2O_5$. According to R. de Forcrand, the white crystals of sodium pyrosulphite have a heat of formation (2S,5O,2Na)=174·2 Cals.; $(2SO_{2gas},Na_2O_{solid})$=54·9 Cals.; and $(SO_{2gas},Na_2SO_{3solid})$=9·4 Cals.; a heat of soln. of one part of salt in sixty parts of water −2·62 Cals. at 10°; and a heat of neutralization of 14·23 Cals. P. J. Hartog said that when freshly prepared the salt can be kept in an atm. of nitrogen, and it undergoes a polymeric transformation attended by the evolution of 2·74 Cals., forming—possibly—$(Na_2S_2O_5)_2$. P. Walden measured the eq. electrical conductivity, λ, of the soln. for a mol of the salt $Na_2S_2O_5$ dissolved in v litres of water at 25°:

v . .	32	64	128	256	512	1024
λ .	67·9	72·3	75·0	76·0	74·8	69·2

which is taken to show that sodium pyrosulphite is the salt of a dibasic acid. C. Schultz-Sellack found that the salt gradually loses sulphur dioxide when exposed to air, and it passes into normal sodium sulphate; D. Gernez, that in a current of carbon dioxide the aq. soln. loses sulphur dioxide; and G. A. Barbaglia and P. Gucci, that when the sat. soln. is heated in a sealed tube at 150°, sodium sulphate and sulphur are formed. According to H. Endemann, when heated to 80° for a long time it loses a mol. of sulphur dioxide; if rapidly heated, it forms sulphur and its dioxide: $2Na_2S_2O_5=2Na_2SO_4+S+SO_2$; and when heated with alcohol, it loses sulphur dioxide. F. Förster and co-workers gave for the solubility of sodium pyrosulphite, in grams per 100 grms. of soln.:

	−8·5°	−2·0°	0°	3·5°	8·6°	15·0°	40·2°	59·2°	85·0°	97·2°
$Na_2S_2O_5$.	24·75	30·45	32·90	37·70	38·65	39·16	41·56	44·29	47·89	49·06
	$Na_2S_2O_5.6H_2O$				$Na_2S_2O_5$					

For the solubility of the heptahydrate, they gave 32·45 at 1·2°; 31·25 at 0°; 26·15 at −5·0°; 23·77 at −9·0°; and 23·45 at −9·3°. The results are plotted in Fig. 68. The anhydrous salt is stable between 5·5° and the b.p. of the soln.; the *heptahydrate*, $Na_2S_2O_5.7H_2O$, is stable between 5·5° and the eutectic temp. −9·05°; and the *hexahydrate*, $Na_2S_2O_5.6H_2O$, is metastable between 3·8° and −9·79°. There were indications of a *trihydrate*, $Na_2S_2O_5.3H_2O$; and of a *tritahydrate*, $Na_2S_2O_5.\frac{1}{3}H_2O$. Cryoscopic observations show that in aq. soln. the salt is hydrolyzed $S_2O_5''+H_2O\rightleftharpoons 2HSO_3'$. N. W. Sokoloff, and R. Otto supposed that a soln. of iodine in one of potassium iodide furnishes the dithionate, but it is rather sodium hydrosulphate and iodide that is formed as shown by L. Bourgeois and W. Spring, A Colefax, L. P. de St. Gilles, and M. J. Fordos and A. Gélis. When the soln. of the pyrosulphite is boiled with sulphur, V. Faget observed that the salt is transformed into hyopsulphite and trithionate, which are, in turn, decomposed into sulphate, and sulphurous acid.

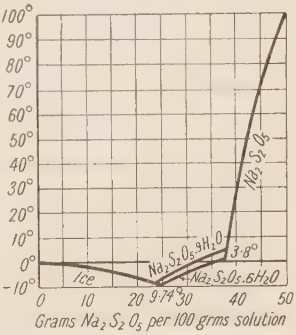
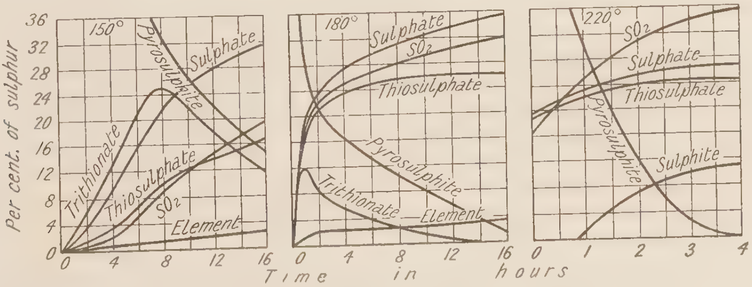


FIG. 68.—Solubility of Sodium Pyrosulphite.

J. S. Muspratt[4] prepared **potassium pyrosulphite,** $K_2S_2O_5$, by passing sulphur dioxide into the hot, sat., aq. soln. until effervescence has ceased, and the green soln. deposits crystals of the salt which are then washed with a little alcohol, and dried between bibulous paper. A. Boake and F. G. A. Roberts obtained the pyrosulphite industrially by passing sulphur dioxide into a boiling soln. of potassium sulphate mixed with calcium hydroxide until the sp. gr. is 1·460, and cooling the liquid. The subject was discussed by J. Fornell. P. Groth, and J. C. G. de Marignac said that the monoclinic plates are stable in air, and have the axial ratios



FIGS. 69, 70, and 71.—Percentage of Different Forms of Combined Sulphur present at Different Temperatures.

$a : b : c = 1{\cdot}4650 : 1 : 1{\cdot}2222$, and $\beta = 131° 43'$. A. H. Röhrig represented the thermal decomposition of the salt by: $2K_2S_2O_5 = 2K_2SO_4 + 4S + SO_2$; and A. Geuther said that the changes which occur when the salt is heated are almost the same as those which occur when the hydrosulphite is heated. F. Förster and G. Hamprecht found that when heated for different periods of time, at different temp., potassium pyrosulphite furnishes the proportions of the different substances indicated in Figs. 69, 70, and 71. Between 220° and 700°, they obtained, in unit time:

	SO_2	S_2O_3''	SO_4''	S	S''	$S\;''$	SO_3''
250° . . .	35·1	26·9	27·9	1·0	—	—	7·4
300° . . .	32·3	26·3	36·0	3·4	—	—	1·5
360° . . .	31·0	23·1	38·5	7·0	—	—	0·4
410° . . .	28·2	13·7	43·1	14·8	—	—	—
500° . . .	31·7	—	46·8	6·1	3·3	10·6	—
600° . . .	30·3	0·4	47·9	12·1	2·9	7·3	—
700° . . .	31·6	—	46·7	11·0	3·5	5·7	—

F. Förster and G. Hamprecht found that crystalline potassium pyrosulphite begins to break down at about 150°; and at the beginning, the reaction $2S_2O_5'' \rightarrow S_3O_6'' + SO_4''$ (i) occurs; with rising temp. less and less trithionate is formed, and is no longer recognizable at 220°. The aq. soln. of the yellow product form a colourless soln. of trithionate. With a rise of temp. above 150°, the reaction $3S_2O_5'' \rightarrow S_2O_3'' + 2SO_4'' + 2SO_2$ (ii) sets in, and above 250°, this is the main reaction. The reaction $S_2O_5'' \rightleftharpoons SO_3'' + SO_2$ (iii) sets in above 200°; if the partial press. of the sulphur dioxide is low the heat of the reaction is: $K_2SO_3 + SO_2 = K_2S_2O_5 + 26{\cdot}8$ Cals. at 220°, and the dissociation press. p is $\log p = -25800/4{\cdot}571T + 1{\cdot}75 \log T + 3{\cdot}3$. There is also a series of consecutive reactions: $S_3O_6'' \rightarrow SO_4'' + SO_2 + S$ (iv) which set in as soon as the conc. of the trithionate reaches a certain limit, and vanishes before all the pyrosulphite has decomposed. The higher the temp., the less the proportion of S_3O_6''. There is also the reaction $2S_2O_3'' + SO_2 \rightarrow 2SO_4 + 3S$ (v), which is the more marked the higher the partial press. of the sulphur dioxide; and the higher the temp. At 220° in a closed vessel, or from 250° to 440° this reaction completes the decomposition of the pyrosulphite. Both the reactions: $4S_2O_3'' \rightarrow 3SO_4'' + S_5'$ (vi) and $4SO_3'' \rightarrow 3SO_4'' + S''$ (vii), or the summated reaction: $2S_2O_5'' \rightarrow 2SO_4'' + S + SO_2$ (viii) occur. Reaction (vi) appears above 400°, provided the temp. is attained before all the thiosulphate has decomposed by (v). The reaction (vii) has a perceptible velocity at 550°. The thermal decomposition of sodium pyrosulphite is similar, but the proportions of the different products are different. The heat of dissociation: $Na_2S_2O_5 \rightleftharpoons Na_2SO_3 + SO_2$, is smaller than is the case with the potassium salt, and the dissociation press. is therefore greater. M. Berthelot gave 184·7 Cals. for the heat of formation from its elements; and 19·20 Cals. from 2 mols each of sulphur dioxide and potassium hydroxide in aq. soln. at 13°; while the heat of soln. in dil. potash-lye is 15·20 Cals. at 13°. A. Lumière and A. Seyewetz found that the moist salt does not change much in moist air, and that the dil. soln. is oxidized twenty times more slowly than the corresponding sodium salt. A. Röhrig observed that the salt smells of sulphur dioxide when it is rubbed in a mortar, and that the powder loses sulphur dioxide in vacuo. F. Förster and co-workers found the solubility of potassium pyrosulphate, in grams per 100 grms. of soln., to be:

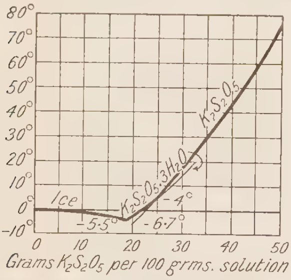


FIG. 72.—Solubility of Potassium Pyrosulphite.

	−6·0°	−3·0°	0°	10°	22·0°	50·2°	94·0°
$K_2S_2O_5$.	19·27	20·65	22·20	26·52	31·82	42·79	55·51

and for the solubility of the *ditritahydrate*, $K_2S_2O_5.\frac{2}{3}H_2O$:

	−0·4°	1·0°	5·0°	10·1°	12·2°	15·0°	20·1°
$K_2S_2O_5$.	21·50	22·75	23·75	27·25	28·37	30·05	33·20

The eutectic temp. for the anhydrous salt is −5·5°, and for the ditritahydrate, −6·7°. The transition temp. is near 4·0°. Between −4° and +4°, **potassium tetrahydrosulphitopyrosulphite**, $K_2S_2O_5.4KHSO_4$, crystallizes out of the soln. Cryoscopic observations show that the pyrosulphites are hydrolyzed in aq. soln., $S_2O_5'' + H_2O = 2HSO_3'$. The salt is slowly dissolved by water, and by alcohol, but is insoluble in ether.

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§ 27. Sulphur Trioxide

The seventeenth-century writer, Basil Valentine,[1] said that when calcined copper vitriol is heated in a retort with a receiver, there first appears a white spirit which is *mercurius philosophorum*, and this is followed by a red spirit which is *sulphur philosophorum*. Albertus Magnus, in the twelfth century, said that *sulphur philosophorum* is not true sulphur, but is rather the spirit of vitriol—*scilicet est spiritus vitreoli romani*. In the seventeenth century, also, N. Lemery obtained the white spirit by heating iron vitriol, and the term *sal philosophorum*—philosopher's salt—came to be applied to the white sublimate as distinguished from the oily liquid *oleum sulphuris,* that is, sulphuric acid—*vide infra.* In 1775, J. C. Bernhardt described the preparation of the white sublimate by heating fuming sulphuric acid, and he called it *sal volatile olei vitrioli.* The white mass obtained as a sublimate when fuming sulphuric acid is heated was called *oleum glaciale vitrioli,* and regarded by J. C. Dollfus, and A. F. de Fourcroy as a compound of sulphuric acid with sulphur dioxide; by J. J. Winterl, as a compound with oxygen; and by F. C. Vogel, as sulphuric acid associated with very little water and a small, unweighable quantity of a spirit or principle. The nature of this product was demonstrated by J. W. Döbereiner, C. G. Gmelin, A. Ure, A. Bussy, C. W. Scheele, and L. B. G. de Morveau; and the composition, by the work of A. L. Lavoisier, J. J. Berzelius, J. B. Richter, C. L. Geoffroy, L. B. G. de Morveau, M. H. Klaproth, C. F. Bucholz, C. L. Berthollet, R. Weber, etc. The results show that the *sal volatile olei vitrioli* is **sulphur trioxide,** SO_3.

The formation and preparation of sulphur trioxide.—The formation of a small proportion—about 2 per cent.—of sulphur trioxide during the combustion of sulphur in air was observed by G. Lunge,[2] J. H. Kastle and J. S. McHargue, W. Hempel, etc.; and H. Giran observed that the proportion of sulphur trioxide formed increases as the press. is raised, Fig. 32—*vide supra,* the combustion of sulphur. R. G. W. Norrish and E. K. Rideal observed that the formation of trioxide becomes appreciable at 305°, and increases rapidly as the temp. is raised. The formation of sulphur trioxide along with the dioxide, during the roasting of pyrites, was discussed by A. Scheurer-Kestner, F. Wöhler, G. Lunge and F. Salathé, F. Bode, and F. Muck. The sulphur in coal-gas was shown by W. C. Young, C. Heisch, M. Dennstedt and C. Ahrens, and G. W. Wigner to be largely converted into the trioxide as the gas burns—*vide supra,* the combustion of sulphur.

As previously indicated, sulphur trioxide is a product of the decomposition of sulphur dioxide by heat, light, or electric sparks. H. Buff and A. W. Hofmann[3] observed that the trioxide is formed when a mixture of sulphur dioxide with half its vol. of oxygen, is exposed to the spark discharge, and P. de Wilde, and M. Poliakoff obtained a similar result with the silent discharge. H. St. C. Deville said that a state of equilibrium is established which prevents the completion of the reaction, but if the sulphur trioxide be removed as fast as it is formed, by absorption in conc. sulphuric acid, the reaction can be completed. M. Berthelot said that some sulphur heptoxide is produced at the same time—*vide supra,* the oxidation of sulphur dioxide for the formation of sulphur trioxide by the action of light, and various agents on mixtures of oxygen and sulphur dioxide. I. Guareschi obtained vortex rings of sulphur trioxide from fuming sulphuric acid and air.

In 1831, P. Phillips[4] said: "I do affirm that an instantaneous union of sulphur dioxide and oxygen of the air can be effected by passing a mixture of sulphur dioxide with a sufficient supply of air through tubes containing finely-divided platinum, heated to a strong yellow heat." Shortly afterwards, G. Magnus observed that a mixture of sulphur dioxide with half its vol. of oxygen is gradually condensed to sulphuric acid in the presence of water, but much more quickly in the presence of heated platinum, particularly of the spongy variety. He also observed that some trioxide is formed when the mixed gases are passed through a tube containing broken glass at a dull red-heat. J. W. Döbereiner also observed the condensation of the gaseous mixture to fuming sulphuric acid by hygroscopically moist platinum black. In 1846, J. T. Jullion recommended asbestos covered or coated with platinum or other catalytic or contact substance heated to 20°–480° for various catalytic reactions, but not specifically for oxidizing sulphur dioxide by air. J. C. Schneider made a working model of an apparatus for oxidizing sulphur dioxide and subsequently converting the trioxide into sulphuric acid. The process was reported upon by A. Payen—co-operating with J. B. A. Dumas, and J. Pelouze. F. Wöhler, and F. Mahla observed that the oxides of chromium and copper, at a dull red-heat, oxidized sulphur dioxide mixed with air to form sulphur trioxide. The contact catalyst employed is not known. Many contact agents other than platinum were proposed. R. Laming, for instance, impregnated pumice with manganese dioxide ; C. Blondeau, argillaceous and presumably ferruginous sand ; T. von Artner, a ceramic body ; W. Hunt, silica ; H. G. C. Fairweather, zeolites impregnated with a metal oxide ; A. M. G. Sébillot, heated pumice-stone ; G. Robb, pyrites-cinders ; W. H. Thornthwaite, and B. Lambert, iron and chromium oxides ; A. Trueman, and A. E. Schmersahl and J. A. Bouck proposed several other oxides ; and H. W. Deacon, copper sulphate.

The reaction is symbolized $2SO_2+O_2\rightleftharpoons 2SO_3$ and it is reversible, and exothermal from left to right. This means that as the temp. is raised there will be a tendency to absorb heat, and this can occur only by the dissociation of the trioxide. Hence, the higher the temp. the worse the yield of sulphur trioxide. The greater the activity of the catalyst the greater the yield because its working temp. is lower. The value of the equilibrium constant K_c will therefore be $[SO_2]^2[O_2]=K[SO_3]^2$ when the conc. are expressed in mols per litre. At temp. in the vicinity of 727°, the initial and final values of the ratios $2SO_2 : O_2 : N_2$ are indicated in Table V.

TABLE V.—EQUILIBRIUM CONDITIONS IN THE SYSTEM $2SO_2+O_2\rightleftharpoons 2SO_3$.

Initial.	Final (Mols × 10^4).			Per cent. Conversion.	$K_c\times 10^3$.
$2SO_2 : O_2 : N_2$.	SO_2.	SO_3.	O_2.		
0·21 : 1 : 0 . .	31·9	47·0	161	59·6	34·9
0·54 : 1 : 0 . .	199	230	248	53·6	3·51
0·62 : 1 : 0 . .	15·9	17·5	18·2	52·2	3·59
1·14 : 1 : 0 . .	218	174	85·8	44·4	3·44
1·20 : 1 : 0 . .	369	287	130	43·7	3·48
1·32 : 1 : 0 . .	260	192	88·7	42·3	3·67
1·68 : 1 : 0 . .	388	230	69·8	37·2	3·50
3·97 : 1 : 0 . .	379	99·5	10·5	20·8	3·67
1·23 : 1 : 3·76 .	91·2	50·0	32·5	35·3	3·62
1·31 : 1 : 3·76 .	339	175	109	34·1	3·54
1·55 : 1 : 3·76 .	337	161	80·4	32·3	3·52

M. Bodenstein and R. Pohl represented their results at T° K., by $\log_e K_c = -10373T^{-1}-2{\cdot}222\log_e T+14{\cdot}585$. When the conc. is expressed in partial press., $p^2{}_{SO_2}p_{O_2}=K_pP^2{}_{SO_3}$, where K_c at 400° is $7{\cdot}81\times 10^{-8}$, and $K_p=4{\cdot}32\times 10^{-6}$, F. Pollitzer gave $\log K_p=9430T^{-1}-1{\cdot}75\log T-3{\cdot}4$. F. Haber proposed the form $K_pP_{SO_2}P^{\frac{1}{2}}_{O_2}=P_{SO_3}$, for the equilibrium relation so as to give more convenient values for the equilibrium constant. If a denotes the initial percentage amount of sulphur dioxide by vol. ; b, that of oxygen ; and x, the amount of oxidation, then, when equilibrium is attained, $\frac{1}{2}ax$ vol. of oxygen will have disappeared, and the partial press. will be $p_{SO_2}=a(1-x)/(100-\frac{1}{2}ax)=p_{SO_3}=ax/(100-\frac{1}{2}ax)$; and $p_{O_2}=(b-\frac{1}{2}ax)/(100-\frac{1}{2}ax)$, so that the equilibrium relation takes the form:

$$k_p=\frac{x}{1-x}\left(\frac{b-\frac{1}{2}ax}{100-\frac{1}{2}ax}\right)^{-\frac{1}{2}}$$

The values of k_p obtained by G. Bodländer and K. Köppen, with those of R. Knietsch (in brackets), are as follow :

	450°	500°	515°	533°	600°	610°	700°	800°	900°
k_p .	(187·7)	(72·3)	65·4	28·4	(14·9)	10·6	4·84	1·81	0·57

M. Bodenstein's values for k_p, and for Q_p Cals. calculated from the equation $d(\log_e K_p)/dT=Q_p/2RT^2$, are :

	528°	579°	627°	680°	727°	789°	832°	987°
k_p . .	31·3	13·8	6·54	3·24	1·86	0·956	0·627	0·358
Q . .	22·8(600°)				22·6(800°)			

M. Bodenstein and R. Pohl's results can be represented by the expression $\log_{10} K_p = 5186{\cdot}5T^{-1} + 0{\cdot}611 \log T - 6{\cdot}7497$; F. Haber suggested $\log_e k_p = 4747{\cdot}3T^{-1} - 20{\cdot}4$ on the assumption that the heat of the reaction is constant. In order to make the values calculated from F. Haber's equation harmonize with those from M. Bodenstein and R. Pohl's equation, it is necessary to increase F. Haber's values of T by 9 units at 400°, 5 units at 520°, and by 2 units at 600°. There is a fair agreement between the values of k_p obtained by R. Knietsch and by G. Bodländer and K. von Köppen; but not with those of M. Bodenstein and R. Pohl. Some measurements were also made by R. Lucas, A. Geitz, C. G. Fink, D. Alexéeff, and W. K. Lewis and E. D. Ries. A. F. Benton discussed the kinetics of reactions in flow systems. R. Kranendick observed that the rate of decomposition of sulphur trioxide at 859° gave a velocity constant k in harmony with a termolecular reaction $dC/dt = kC^3$, but not with a bi- or uni-molecular reaction.

Three vols. of the mixed gases furnish two vols. of the trioxide; pressure tends to make the vol. smaller, and as the system adjusts itself to the increased press. it has a tendency to form more sulphur trioxide. In practice, the increased yield obtained by increasing the press. is not sufficient to make the extra cost worth while. R. Knietsch showed that an increase of press. and dilution with inert gases act in opposite directions. Thus, at 430° with a mixture of 7·21, 10·44, and 82·35 per cent. of sulphur dioxide, oxygen, and nitrogen respectively, there was a 98·9 per cent. conversion at atm. press. and a 99·50 per cent. conversion at 5·3 atm. press. At 490°, with a mixture of 6·60, 11·30, and 82·10 per cent. of sulphur dioxide, oxygen, and nitrogen, the per cent. conversion at atm. press. was 93·80, and at 0·31 atm. press., 90·85 per cent. R. Frank proposed working the contact process under a press. of 100 atm.

R. Knietsch measured the rate of oxidation of sulphur dioxide by passing the mixed gases at different speeds, V litres per minute, over 0·5 grm. of the platinum catalyst, and expressed the result in grams of sulphur dioxide converted per minute per gram of platinum:

	410°	430°	450°	480°	515°	
V	0·3	1·0	2·5	7·5	20·0	
Conversion . . .	100	97·5	94	87·5	7·3	per cent.
Grams SO_2 converted .	0·15	0·37	0·90	2·5	5·6	

This shows that the catalytic activity or the rate of conversion increases more and more rapidly as the temp. rises; but the percentage conversion falls more rapidly. The curves, Fig. 73, show that as the temp. rises, the percentage conversion rises rapidly at first, then reaches a maximum, and the curve then takes a downward slope towards the region of higher temp. The right-hand branches of the curves lie close together, showing that the percentage conversion thus becomes more and more dependent on temp., and less on the relative weights of gas and catalyst; the speed of conversion is so high that the results are nearly all the same. At these high temp. there is a large excess of catalytic activity. The curves, Fig. 74, by R. Knietsch, represent the relation between the amount of platinum or the

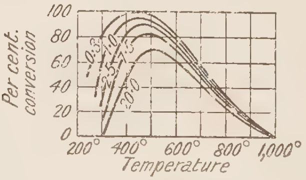


Fig. 73.—The Relation between Temperature and the Rate of Oxidation.

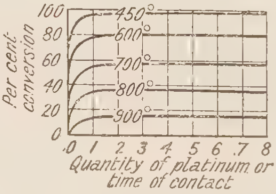


Fig. 74.—Relation between Conversion and Times of Reaction at various Temperatures.

time of contact with a constant quantity of platinum. They show the time required to obtain a certain percentage conversion at a given temp.

The intermediate compound theory is a convenient way of explaining the action of catalytic agents—*vide* **1.** 8, 6—but it does not work so well with platinum. As indicated in connection with sulphur dioxide, H. Wieland found that palladium black, in the absence of oxygen, will oxidize moist sulphur dioxide; whilst traces of water are necessary for the reaction between oxygen and sulphur dioxide. It has therefore been suggested that in the catalysis of the oxidation process, the water is alternately reduced and re-formed by the cyclic reactions $SO_2+H_2O=SO_3+H_2$, and $2H_2+O_2=2H_2O$. C. Engler and L. Wöhler supposed that a transient platinum oxide acts as a carrier of oxygen—at first, it was supposed that platinum dioxide is formed, and later, platinum monoxide. L. Wöhler, however, showed that platinum monoxide is reduced to the metal by sulphur dioxide before the oxidation of the sulphur dioxide has well begun; and that the catalytic action of the platinum oxide is only about one-fifth of that of the metal. L. Duparc and co-workers inferred that in the oxidation of sulphur dioxide, with rhodium or platinum as catalyst, intermediate compounds of oxygen with the catalyst are formed. M. Bodenstein argued that no oxide whose formation is endothermic can act as intermediate oxide; a platinum oxide may be formed and dissolve in the platinum, and the sulphur dioxide may dissolve in the metal. The function of the catalyst is then to form a solid soln. in which the reaction proceeds.

Measurements of the velocity, made by M. Bodenstein and C. G. Fink, showed that the reaction did not proceed as a termolecular gas reaction might be expected to do; but at the moment t, the speed was directly proportional to the amount of dioxide present in the system, and inversely proportional to the sq. root of the amount of trioxide formed, that is, $dx/dt=k(a-x)x^{-\frac{1}{2}}$. At 248°, the conc. of the oxygen had no appreciable influence within very wide limits; but if less oxygen was present than is represented by the ratio $2SO_2 : O_2$, the value of k was no longer constant, and the rate of the reaction became abnormally slow. It is assumed that the trioxide formed accumulates on the surface of the platinum by adsorption, and the reacting gases have to penetrate this layer before they can react; and, since the amount of a substance adsorbed depends on the conc., the higher the conc. of the trioxide the greater its retarding effect on the reaction. This is in accord with the observed results. The temp. coeff. of the reaction is about 1·22 for every 10°; and the coeff. is usually of the same order for reactions in soln. catalyzed by colloidal metals, but for reactions in soln. the speed of the reaction is nearly doubled for every 10° rise of temp. It is therefore assumed that reactions catalyzed at a platinum surface are retarded by some factor not present with reactions in soln. This factor is not adsorption, because adsorption is an instantaneous process; rather is the retardation caused by the diffusion of the gases through the adsorbed layer on the surface of the catalyst. The temp. coeff. of diffusion processes is usually much lower than the value for typical chemical reactions. According to this hypothesis, the catalytic activity of platinum is attributed to the adsorption of the reacting gases into the body of the metal, or to the reaction taking place in the condensed layer formed on the surface of the metal. In some cases of catalysis—*e.g.* the oxidation of ammonia—C. S. Imison and W. Russell showed that there is a drastic pitting and sprouting over the whole surface.

The destruction of the catalytic activity by the overheating of the catalyst is a result of the almost complete suppression of the power of adsorption. The state of the surface of the catalyst, therefore, determines the extent and accessibility of the reacting gases. The various methods of preparing catalysts are usually directed towards making the adsorbing surface as large as possible. They range from mechanical comminution to the deposition of the catalyst in an extreme state of subdivision on a more or less porous, inactive support. J. T. Jullion recommended asbestos as a carrier for the platinum in various catalytic reactions, although not specifically for oxidizing sulphur dioxide. The long-fibred asbestos, well teased out, has given good service in industrial plants lasting from ten to a dozen years. R. Piria used calcined quartz and also pumice-stone as carrier for platinum; and H. N. Holmes and co-workers, silica gel. Magnesium sulphate was recommended by M. Schröder, and the Badische Anilin- und Sodafabrik recommended using oxide of iron, copper, or chromium as a carrier for platinum. C. Ellis recommended mixing platinum with an oxide, one which is capable of absorbing a large volume of sulphur dioxide at 450°–540°.

About 1875, W. S. Squire, and R. Messel used platinized pumice as the catalytic agent for the oxidation of sulphur dioxide, and they noticed that the catalyst gradually lost its activity owing to the accumulation on it of such impurities as flue-dust, when gases from the roasting of sulphides, etc., were used. R. Knietsch showed that arsenic in the burner gas was the most harmful of the impurities. It acts by permanently destroying the efficiency of platinum as a catalyst; and once the platinum is contaminated seriously, it has to be recovered and the arsenic separated. E. B. Maxted and A. N. Dunsby studied the poisoning of the catalyst by arsenic; and the retarding effect is proportional to the concentration of the arsenic per gram of platinum:

Arsenic .	0	0·00071	0·00143	0·00214	0·0050	0·0079	0·0286 grm.
SO_2 oxidized .	15·13	12·17	8·53	6·77	6·15	5·60	4·03 per cent.

R. Knietsch found that other substances have a deleterious action—*e.g.* antimony, chlorine, iodine, hydrogen chloride, silicon tetrafluoride, selenium, tellurium, sulphur, lead sulphate, etc. There are two ways in which these injurious agents can act on the platinum. There is first the *mechanical action* by the deposition of solid matter on the catalyst which renders the platinum more difficult of access to the reacting gases. There is also what is now known as a *specific poisoning action* owing to which the catalyst becomes inactive. The action of arsenic, antimony, tellurium, selenium is permanent and specific; the action of chlorine and hydrogen chloride is temporary and specific; while the other substances act mechanically. C. Opl supposed that the specific, poisoning action of arsenic is due to the formation of a glassy film of arsenic sulphite on the surface; while M. Bodenstein and C. G. Fink suggest that the inactivity may be due to the decreased adsorption of gases on the surface of the catalyst. E. J. Russell and N. Smith showed that if the gases be thoroughly dried with phosphorus pentoxide, the reaction is so slow that only a slight change was observed after 24 hrs.' contact with platinum at 400°–450°. R. Knietsch observed that at 460°, mixtures with 7·2 and 6·6 per cent. of sulphur dioxide containing respectively 13·5 and 26·7 per cent. of water-vapour showed a respectively 96·4 and 96·8 per cent. oxidation. C. L. Reese also observed but little effect when tried on a small scale. On a large scale, however, all are agreed that the effect of steam is injurious. The subject was also discussed by F. Meyer, G. C. Stone, and G. Lunge and G. P. Pollitt.

R. Schwarz and M. Klingenfuss said that X-rays activate the platinum used as catalyst in the oxidation of sulphur dioxide, and so increase the yield of trioxide. At 400° the yield of sulphur trioxide is increased from 94·6 to 95·9 per cent., and at 260° from 35 to 51 per cent., after treatment of the platinum catalyst. The activation is not permanent, but gradually decreases, and has practically disappeared after the catalyst has been in use for 24 hrs. The phenomenon is probably due to the decomposition of small amounts of water with the production of a specially active oxygen on the platinum surface. G. L. Clark and co-workers showed that X-rays do not activate the platinum catalyst in the oxidation of sulphur dioxide when it is exposed to the radiation in dry air; but in a moist atm. containing 0·013 part of water per 1 part of dry air, it was activated, and an increase in conversion obtained over the first period of use. The activity then fell to a minimum, and finally returned to its normal value before irradiation. Subsequent irradiation gave less activation and a slower return to the normal.

The decreased effect of X-rays after the first exposure is regarded as being due to the building up of a film of sulphuric acid which is not easily ionized by the radiation. R. G. Y. de Sotto proposed to activate the gases by exposing them to radium rays or ultra-violet light. J. E. Maisin found that in the oxidation of sulphur dioxide exposed to the α-particles from radium, sulphur trioxide is the principal product; no persulphuric anhydride was observed. The ratio of the number of molecules disappearing from the gaseous phase to the number of ions produced is about 1·5. Assuming that the reaction proceeds: $2SO_2+O_2=2SO_3$, this means that each pair of ions produces a mol. of sulphur trioxide.

The catalytic action of platinum for the oxidation of sulphur dioxide was found by L. Wöhler and co-workers to be much superior to both palladium and iridium. With 10 grms. of catalytic mass containing 1·4–1·5 per cent. of metal, and a mixture of one part of sulphur dioxide with 2·5 parts of air passing at the rate of 176–179 c.c. per minute, they found that the possible and observed conversions at different temp. were:

			450°	550°	650°	750°	
Conversion	possible		96	80	56	32	per cent.
	observed	platinum	96·2	79·9	47·9	21·6	,,
		iridium	27·0	67·1	42·8	19·2	,,
		palladium	0·5	23·4	40·0	22·5	,,

If the rate of passage of the mixed gas be augmented, the lower activities of iridium and palladium are accentuated. P. Wenger and C. Urfer also found rhodium to be inferior to platinum. According to G. R. Levi and M. Faldini, the presence of 10 per cent. of either of these metals in the platinum used in the catalytic preparation of sulphur trioxide from dioxide and air causes a marked diminution in the yield, probably owing to the ability of rhodium and iridium to form moderately stable oxides, especially sesquioxides; osmium produces a similar but less pronounced effect, whereas palladium or ruthenium in the same proportion increases the yield. A. Classen patented the use of ferrochromium, ferrovanadium, ferromolybdenum, ferrosilicon-manganese, and ferrosilicon-aluminium; these alloys were found to be superior to manganese and tungsten. F. A. Fahrenwald said that alloys of silver or gold with platinum or molybdenum are active enough to be of technical importance. The Ellis Forster Co. proposed the use of mixtures of selenium and tellurium as catalytic agents.

The use of ferric oxide has played an important part in the manufacture of sulphur trioxide by the contact process; it is much inferior to platinum. Thus, R. Knietsch found that at about 550°, when 0·5 grm. of platinum is converting 30 litres of gas per minute to the extent of about 70 per cent., a much larger amount of ferric oxide can convert only half a litre of gas per minute to the extent of 46 per cent. The use of ferric oxide as a catalytic agent was investigated by G. Lunge and co-workers. They found that the percentage conversion was not much affected by changing the concentration from 2 to 12 per cent., but with higher concentrations the yield was reduced. The mixture of gases should be dried by conc. sulphuric acid. If moisture be present, the activity of the catalyst is reduced; the moisture adsorbed when ferric oxide is exposed to air also renders the catalyst less active. The more intense drying by phosphorus pentoxide was shown by E. J. Russell and N. Smith, and F. W. Küster to be harmful. The addition of copper oxide was found to be favourable to the conversion. Any arsenic trioxide present in the sulphur dioxide, produced, say, by the roasting of pyrites, is retained by the heated ferric oxide, and the presence of the arsenic oxide makes the catalyst more efficient. A 70 per cent. yield could be obtained at 625° by the use of ferric arsenate as a catalyst; and arsenic pentoxide alone acts as a catalyst with an optimum temp. of 675°. The so-called promoter action or the activation of catalysts was studied by R. N. Pease and H. S. Taylor. E. Berl, and K. Reinhardt studied the activity of arsenic pentoxide as a catalyst, and found it to be comparable with that of ferric oxide or of vanadium oxide. The action of ferric oxide as a catalyst is perceptible at 400°; below 600°, the ferric oxide has only a slight activity, and above 620°, the activity decreased. The optimum temp. is between 600° and 620°; and there is then approximately a 70 per cent. conversion. In practice, however, a conversion of 40 per cent. with a burner gas containing 5–7 per cent. of sulphur dioxide is considered to be a good result; but, according to F. Haber, it is doubtful if the equilibrium yield has ever been attained because a long contact with the catalyst is needed for equilibrium. G. Keppeler and J. d'Ans found the optimum temp. to be 629° for a mixture containing 2 per cent. of SO_2, and there was a 72·5 per cent. yield; with 3 per cent. SO_2, the optimum temp. was 640°; with 4 per cent., 650°; and with 7 per cent., 665°. The yields in the last two cases were respectively 65·0 and 53·2 per cent. A number of attempts have been made to improve the catalytic activity of ferric oxide. Thus, K. Albert heated a mixture of ferric oxide with oxide of barium or strontium. The catalysis begins at 400°, and gives a 94 per cent. conversion at 450°; nor is the product so sensitive to moisture as ferric oxide alone.

The catalytic action of ferric oxide has been explained by assuming that ferric sulphate or a basic ferric sulphate is alternately formed and decomposed, since ferric sulphate decomposes in the same temp. range as ferric oxide is active as a catalyst: $2Fe_2O_3+6SO_2+3O_2=2Fe_2(SO_4)_3$; $Fe_2(SO_4)_3=Fe_2O_3+3SO_3$. G. Keppeler and J. d'Ans measured the partial press. of the trioxide produced by the dissociation of ferric sulphate. Ferric oxide begins to absorb both sulphur dioxide and oxygen at 230°, and is rapid enough at 500° to enable the equilibrium conditions to be determined. It was shown that the conc. of the sulphur trioxide is always higher than that corresponding with the equilibrium value for the dissociating ferric sulphate; this means that sulphur trioxide forms first and combines afterwards. Below 640°, the rate of formation of the trioxide is far greater than the rate of formation of the sulphate; and sulphur dioxide does not act on ferric oxide below 600°, and at higher temp., the reaction is very slow. On the other hand, the gas is adsorbed by the ferric oxide to about the same extent as with platinum. Hence, they concluded that the chemical transformation of ferric oxide to a sulphate has very little to do with its catalytic action. It was therefore assumed that the catalytic activity of ferric oxide is connected with adsorption as in the analogous case with platinum. F. Wöhler and co-workers, and W. Plüddemann and co-workers found that the catalytic activities of the oxides of iron, chromium, copper, aluminium, cerium, thorium, silicon, and titanium are proportional to their capacities for adsorption. E. Berl arrived at a similar conclusion with respect to the catalytic activity of arsenic pentoxide. K. Reinhardt also studied the catalytic activities of ferric, arsenic, and copper oxides, and of glass, porcelain, and quartz on the oxidation of sulphur dioxide by air.

The use of chromium oxide as a catalyst was examined by F. Wöhler, and F. Mahla in 1852; and it was the subject of a patent by A. C. Matignon and fellow-workers in 1908. The oxide is to be made porous by calcining a compound like ammonium dichromate, chromium nitrate, or chromium oxide mixed with some substance from which a gas is evolved—*e.g.* antimony trichloride or stannic chloride. The temp. required with chromium oxide ranges from 420° to 630°. Patents were also obtained by the Ellis Forster Co., and B. Lambert.

A number of patents have been obtained for the use of vanadium oxide as a catalytic agent, in the hope of obtaining a catalyst insensible to arsenical "poisoning." The Höchst Co. claimed a 84 per cent. conversion at 465° with asbestos impregnated with ammonium vanadate and ignited. The Badische Anilin- und Sodafabrik obtained a number of patents for the use of vanadium pentoxide on an indifferent carrier—say pumice-stone. The General Chemical Co. impregnated kieselguhr; W. A. Patrick and E. B. Miller, A. O. Jäger, silica gel with colloidal metals—Pt, Fe, Ag, Mn, Cu, Co—or nickel vanadate; and A. O. Jäger and J. A. Bertsch, zeolites with the vanadate. The Conidelon Co. used iron vanadates; L. F. Nickell, vanadium silicates; and the F. Bayer Co., silver vanadate. It is said that silver or silver oxide alone has very little action; and that the vanadates of copper, cobalt, manganese, and of several other metals are less active than vanadium pentoxide. It is therefore remarkable that silver vanadate should give a theoretical conversion at 520°. The presence of sodium or potassium salts is said by the Badische Anilin- und Sodafabrik to protect the catalyst from deterioration. The Selden Co. found that vanadium pentoxide operates most efficiently as an oxidizing catalyst if it has been previously heated to 500° so as to make it denser and more crystalline, or even melted at about 660°. According to F. W. Küster, platinum, vanadium pentoxide, and ferric oxide induce for equal temp. the same state of equilibrium between sulphur dioxide, oxygen, and sulphur trioxide. Platinum is the most effective of the three catalysts mentioned, and is the only one of technical importance. Water has considerable influence on the catalytic activity of ferric oxide and vanadium pentoxide. Vanadium pentoxide is not so sensitive as ferric oxide to the deleterious effects of arsenic trioxide. P. Farup recommended ilmenite as catalyst; it is said to give better results than artificial mixtures of iron and titanium oxides. V. Hölbing and H. Ditz recommended cerium oxide and mixtures of rare earths. R. Böhm said that heating the sulphates between 700° and 1000° improves their activity. The Compagnie Parisienne de Couleurs d'Aniline recommended asbestos soaked in phosphoric acid; and M. Bouhard and M. Loyer, oxides of metals of the tantalum group. L. Wolkoff observed that selenium accelerates the oxidation of sulphur to sulphur trioxide.

The history of the subject has been discussed by F. Winteler, the Badische Anilin- und Sodafabrik, R. Knietsch, W. Grillo, M. Feigensohn, R. Messel, F. D. Miles etc. Apparatus for demonstrating the reaction $2SO_2+O_2=2SO_3$ has been devised by C. Winkler, G. B. Frankforter and F. C. Frary, W. R. Hodgkinson and F. K. Lowndes, J. Lang, etc. The efficiency of different catalysts was discussed by B. Neumann and co-workers.

According to J. J. Berzelius,[5] if fuming sulphuric acid be heated in a retort with the neck dipping into a dry receiver, cooled with ice, sulphur trioxide first passes over; and this is followed by its monohydrate, H_2SO_4, so that the receiver must be changed after a while. The retort is best heated from the sides to avoid bumping, or, according to G. Osann, a spirally wound platinum wire should dip in the acid. A. C. Schultz-Sellack said that the product is contaminated with sulphur dioxide, which can be removed only by heating the trioxide for a long time. L. C. A. Barreswil, and H. S. Evans prepared the trioxide by heating conc. sulphuric acid with phosphorus pentoxide; and A. Nobel and G. Fehrenbach, by heating the conc. acid with conc. phosphoric acid, or by passing the vapour of sulphuric acid over a large surface of phosphoric acid.

N. Lemery prepared the trioxide by the dry distillation of ferric sulphate: $Fe_2(SO_4)_3=Fe_2O_3+3SO_3$; T. Graham, by heating to redness antimony or bismuth sulphate in a retort; and A. Schubert, and R. W. Hill, by heating sulphates or hydrosulphates under reduced press. J. J. Berzelius, and P. G. Prelier heated to dull redness a mixture of 3 parts of dry sodium sulphate and 2 parts of conc. sulphuric acid. When the mixture ceases to boil, it is cooled, pulverized, and then heated in a porcelain retort, when the trioxide is formed in brittle, tabular masses. W. Wolters obtained the trioxide by heating sodium pyrosulphate with anhydrous magnesium sulphate, or with conc. sulphuric acid: $Na_2S_2O_7+H_2SO_4=2NaHSO_4+SO_3$.

W. Odling and F. A. Abel obtained the trioxide by heating sulphuryl chloride with silver sulphate: $Ag_2SO_4+SO_2Cl_2=2AgCl+2SO_3$ or $SO_2(SO_4)$. O. von Gruber treated lead chamber crystals with sulphur dioxide and dry air or oxygen. V. Ragosine and P. Dworkowitsch obtained the trioxide from the sulphuric acid residues in the purification of naphtha by mixing it with a metal oxide; heating the product until it solidifies; and passing dry air over the solid residue at 300°–500°. R. Weber purified the trioxide by repeated distillation in a bent glass tube; and warming it 6 or 7 hrs. over phosphorus pentoxide to remove the hydrate. It is then heated until it has almost all melted, and the liquid poured off from the portions still remaining solid.

According to J. C. G. de Marignac,[6] when sulphur trioxide is melted at 18° in a sealed tube a portion of the compound does not fuse until the temp. is raised to near 90°. If the liquid be frozen and again melted a still greater proportion remains solid above 18°. According to A. Smits and P. Schoenmaker, it appears that sulphur trioxide can exist in three *modifications isomériques*—the ice-like form melts easily at about 16·8° at 158·5 mm. press.; the incompletely dried, asbestos-like trioxide melts at 32·5° at 398 mm. mercury press.; and the completely dried, asbestos-like trioxide, at 62·2° and 1743 mm. press.—*vide infra,* Fig. 76. It is assumed that the difference observed by A. Bussy, and G. F. Wach in the m.p. of sulphur trioxide—respectively 25° and 100°—is explained by the existence of these two allotropic varieties. The fusible variety or the ice-like form is now called **α-sulphur trioxide,** the incompletely dried, low-melting, asbestos-like form, **β-sulphur trioxide;** and the thoroughly dried, high-melting, asbestos-like form, **γ-sulphur trioxide.** These results were confirmed by A. C. Schultz-Sellack. On the other hand, R. Weber, and H. Rebs denied the existence of two forms, since, in the absence of moisture, they were unable to prepare the β-trioxide. The β-form was obtained by H. Rebs by contact of molten α-trioxide with moist air; although G. Oddo said that it can be obtained by keeping the α-form in a molten condition while protected from moisture, and he obtained different mol. wts. for the two forms when dissolved in phosphoryl chloride, but D. M. Lichty could not confirm this. D. M. Lichty, and R. Schenck considered that the variation in the thermal expansion with temp.—*vide infra*—agreed with the existence of unusual changes in the nature of sulphur trioxide. A. Berthoud found that if moisture be rigorously excluded from the α-trioxide it does not form a second variety. He said that the alleged β-trioxide is probably a hydrated form of the trioxide which owes its existence to its containing not more than one mol of water to 1000 mols of the trioxide. H. B. Baker observed that drying the α- and β-forms of the trioxide for 20 years lowered the m.p. slightly. Again, M. le Blanc and C. Rühle found that when sulphur trioxide is produced from sulphur dioxide and oxygen by exposure to light while under reduced press., the gaseous trioxide first formed gradually furnishes the solid trioxide. If solid sulphur trioxide be warmed to 17° part of it melts, and with a repetition, the proportion remaining solid above 17° continually increases. Four modifications, *a*, *b*, *c*, *d*, having vap. press. increasing in the order given, are described; *a*, of m.p. 95°–100°, is obtained by condensation of the vap. in the form of needles or delicate membranes; *b*, m.p. 31°, is formed as a tough white mass by condensation at 0°, the generating vessel being at 6°–7°; *c*, at 16·8°; and *d*, at a lower temp. Owing to the general instability of these modifications no separate vap. press. curves could be determined. These results were discussed by A. Smits and co-workers. They studied the irregular behaviour of the trioxide with respect to its m.p. and vap. press. By drying the ice-form over phosphorus pentoxide, so that the velocity of transformation is small, after keeping it for 56 hrs. at 18°, the vap. press. at 0° had diminished by 71·4 mm., and by distillation the vap. press. could be changed continuously from an initial value of 207 mm. to a final value of 22 mm. at 0°. As the vap. press. diminished the initial m.p. first rose and then fell. All these different solid phases belong to the ice-form, since they give melting ranges falling on the continuous three-phase line corresponding with the equilibrium, solid-liquid-vapour, for a dissociable compound. This can be explained by A. Smit's theory of allotropy by assuming that the system, sulphur trioxide, is composed of at least two different kinds of molecules, α and β, which not only change each into the other, but also form a dissociable compound αβ. After intensive drying, equilibrium is reached only slowly. When behaving as a unary system, the ice-form of sulphur trioxide is a little richer in the more volatile pseudo-component than the dissociable compound. A second metastable form, the low-melting asbestos form, and the stable or high-melting asbestos form, show similar phenomena. The theory was discussed by G. N. Lewis, S. B. Mali, A. Smits and P. Schoenmaker, and J. W. Smith.

According to A. Bussy, the liquid trioxide resembles sulphuric acid, and when pure it is colourless, but is often coloured brown by organic matter. The liquid freezes to a mass of colourless, needle-like crystals when cooled below 15°; and, added R. Weber, if free from water, the crystals can be kept many years and remelted without leaving a solid residue. J. C. G. de Marignac said that if the crystals be melted a number of times, the m.p. gradually changes owing to the transformation of α- and β-sulphur trioxide. The β-form occurs as an opaque, colourless mass of needle-like crystals which has the appearance of asbestos. L. B. G. de Morveau found that the **specific gravity** of ordinary solid sulphur trioxide is 1·9546 at 13°; A. von Baumgartner, 1·975; H. L. Buff, 1·90814–1·92118 at 25°; J. C. G. de Marignac, 1·9086 at 20°; R. Weber, 1·940 at 16°; and R. Nasini, 1·9365 at 20°. G. Oddo gave 1·97 for the sp. gr. of the β-trioxide at 20°. For the liquid, A. Bussy gave 1·97 at 20°; and H. L. Buff, 1·8101–1·81958 at 47°. R. Schenck gave 1·914 at 11°; 1·849 at 35·3°; 1·718 at 60·4°; 1·626 at 78·3°; 1·617 at 80·3°; and 1·529 at 100°. D. M. Lichty found for the sp. gr. referred to water at 4°:

	11·8°	15°	20°	25°	30°	35°	40°	48°
Sp. gr. .	1·9457	1·9422	1·9229	1·9020	1·8798	1·8569	1·8324	1·7921

A. Berthoud gave

	20°	25°	30°	35°	40°	45°	50°	55°
Sp. gr. .	1·9255	1·9040	1·8819	1·8588	1·8335	1·8090	1·7812	1·7552

and for the density of the liquid, D_l, and of the vapour D_v,

	98·74°	130·5°	154·6°	182·6°	192·7°	205·3°	212·1°	214·3°
D_l . .	1·541	1·421	1·326	1·182	1·111	1·006	0·921	0·901
D_v . .	0·023	0·047	0·071	0·148	0·194	0·271	0·333	0·365

The results are plotted in Fig. 75, and they show that at the critical temp., 218·3°, the density is 0·633. E. Rabinowitsch gave 44·5 for the mol. vol. D. Balareff studied this subject. N. S. Kurnakoff discussed the spatial relations of the atoms in sulphur trioxide. A. C. Schultz-Sellack found the **vapour density** to be 2·74–2·76 when the calculated value for SO_3 is 2·76 air unity. E. P. Perman found 40·9 at 22·1° and 56·7 mm. press. hydrogen unity; 39·2 at 22·7° and 40·5 mm.; and 40 at 22·8° and 22·1 mm. press. when the theoretical value for SO_3 is 40·03. G. Oddo and A. Casalino found that both forms gave the same vap. density. For the thermal dissociation of the trioxide vapour, *vide supra*. G. Oddo observed that the **molecular weight** calculated from the effect of the α-trioxide on the f.p. of phosphoryl chloride agrees with the formula SO_3, but the β-trioxide has a mol. wt. in agreement with S_2O_6. D. M. Lichty, however, obtained a result in agreement with SO_3 for both forms. G. Oddo and A. Casalino obtained results in agreement with SO_3 for the one form and $(SO_3)_2$ for the other form from cryoscopic observations of soln. in the complex compound $SO_3.2POCl_3$. A. Berthoud found the **surface tension** of the liquid trioxide at 19°, 44·9°, and 78° to be respectively 34·17, 29·17, and 22·63 dynes per cm.; and the mol. **surface energy,** $\sigma(Mv)^{\frac{2}{3}}$, respectively 409·5, 370·2, and 303·9 ergs per cm. The corresponding constant averages 1·79 between 19° and 78°. The coeff. is thus rather lower than the value 2·1 characteristic of normal liquids.

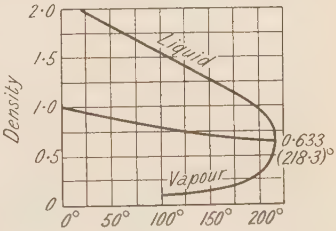


FIG. 75.—The Law of Rectilinear Diameter.

R. Schenck obtained 0·0023 for the coeff. of **thermal expansion** (cubical) between 11·0° and 35·3°; 0·0030 between 35·3° and 60·4°; 0.0031 between 60·4° and 78·3°;

and 0·0028 between 78·3° and 80·3°, and 80·3° and 100°. D. M. Lichty obtained for the coeff. $\beta \times 10^3$,

	11·8°	15°	20°	25°	30°	35°	40°	45°	48°
$\beta \times 10^3$.	0·676	2·005	2·204	2·363	2·466	2·671	2·754	2·805	

for the range 11·8° to 35°, $\beta = 0·002066$; and for the range 25°–48°, $\beta = 0·002665$. R. Schenck said that the α-trioxide attains a constant vol. at 35·3° very slowly whether approached from a higher or a lower temp. This is ascribed to the slowness of the molecular change. D. M. Lichty said that an unusual change does occur with the α-trioxide as its temp. rises ; this is shown by the rapid increase in its coeff. of expansion, and the consequent rapid decrease in its sp. gr. The most rapid change occurs between 15° and 20° ; and the successive increments show a decreasing value with rise of temp. A. Berthoud observed no marked irregularities for the coeff. of thermal expansion :

	20°	25°	30°	35°	40°	45°	50°
$\beta \times 10^3$.	2·23	2·30	2·41	2·63	2·75	2·88	2·80

J. C. G. de Marignac gave 15°–18° for the **melting point** of the α-trioxide ; F. C. Vogel, 12°–19° ; N. W. Fischer, 22°–24° ; A. Bussy, 25° ; H. L. Buff, 29·5° ; H. Rebs, 14·8° ; R. Knietsch, 17·7° ; D. M. Lichty, 16·79° ; and A. Berthoud, 16·85°. J. C. G. de Marignac, and G. F. Wach gave 100° for the m.p. of the β-trioxide ; while G. Oddo said that it begins to decompose slowly at 50° and rapidly passes into the α-form at 100°. H. B. Baker found that sulphur trioxide, dried for 20 years over phosphorus pentoxide, had a m.p. of 61·5°, and α-sulphur trioxide, 15·5° ; while the corresponding values for material not specially dried were 50° and 14·4°. A. Smits and P. Schoenmaker gave 16·8° at 158·5 mm. press. for the m.p. or triple point of α-trioxide ; 32·5° at 398 mm. for the β-trioxide ; and 62·2° at 1743 mm. for the γ-trioxide. G. Oddo found that the β-trioxide begins to give off sulphur trioxide vapour at about 50° ; and J. C. G. de Marignac said that the α-trioxide volatilizes very rapidly at 100°. A. C. Schultz-Sellack found the **vapour pressure** of the α-trioxide to be 200 mm. at 20°. A. Berthoud gave for the vap. press., p mm.,

	24°	30·45°	36·6°	41·4°	42·2°	43·68°	45·4°	47·8°
p .	240·5	352·0	500·0	643·7	678·0	726·5	793·8	887·2

and the results can be represented by the curve $\log p = 10·17 — 2314T^{-1}$. At higher temp., the vap. press., p atm., are :

	98·2°	134·5°	179·9°	192·6°	205·4	211·3	216·9	218·3
p .	9·2	18·7	43·9	55·2	66·9	73·5	80·4	84·0

A. Smits and P. Schoenmaker found the vap. press., p mm., of liquid sulphur trioxide in internal equilibrium to be :

	17·6°	25·3°	35·0°	49·75°	27·1°	65·4°	74·0°	80·9°	90·2°
p .	166·4	270·4	460·7	977·2	1377·2	2041·0	2964·0	3985·5	5794·0 mm.

For the rice-like solid, α-trioxide they gave 43·5 mm. at 0·15° ; 66·0 mm. at 5° ; 98·2 mm. at 10·2 ; and 144·4 mm. at 15·5°. For β-trioxide, they gave 33 mm. at 0·2° ; 49·2 mm. at 5·1° ; 72·3 mm. at 10·1° ; 106·6 mm. at 15·0° ; 162·8 mm. at 20·25° ; 230·1 mm. at 24·85° ; and 334·1 mm. at 30·3° ; and for the γ-trioxide 120 mm. at 30° ; 290 mm. at 40° ; and 650 mm. at 50°. In Fig. 76, *BCDE* represents the vap. press. curve of liquid sulphur trioxide in equilibrium : *AB*, the vap. press. of the ice-like α-trioxide in "inner" equilibrium ; *A′C*, the vap. press. line of the low-melting, asbestos-like β-trioxide in "inner" equilibrium ; and *A″D*, the vap. press. line of the high-melting, asbestos-like γ-trioxide. *B* denotes the m.p. of the α-trioxide ; *C*, that of the β-trioxide ; and *D*, that of the γ-trioxide. The curve *egB* represents the vap. press. of the pseudo-system for the coexistence of mixed crystals containing α-trioxide ; *ghC*, for the pseudo-system containing

β-trioxide; and *hDk*, for the pseudo-system containing γ-trioxide. The X-radiograms of the different forms were found by A. Smits and P. Schoenmaker to be identical, indicating that the X-rays quickly transfer the metastable forms into the stable form. The vap. press. of sulphur trioxide was discussed in connection with fuming sulphuric acid—*vide infra.* A. Purgotti discussed the sublimation of sulphur dioxide. A. C. Schultz-Sellack gave 46° for the **boiling point** at 760 mm.; H. L. Buff, 46°–47°; N. W. Fischer, 52°–56°; E. Mitscherlich, 35°; and R. Weber, 46·2° at 761·6 mm. A. Berthoud obtained by interpolation from his vap. press. measurements 44·52° for the b.p. at 760 mm.; and D. M. Lichty gave 44·88° at 760 mm.; A. Smits and P. Schoenmaker gave 44·8° for the b.p. of α-trioxide at 760 mm. H. M. Vernon found that the b.p. agrees with the assumption that the mol. formula is simply SO_3. R. Schenck gave 216° for the **critical temperature;** and A. Berthoud, 218·3° for the critical temp.; 83·8 atm. for the **critical pressure;** and 0·633 for the **critical density.** M. Prud'homme studied some relations between the critical temp. The **heat of vaporization** is 10·3 Cals. per mol.; M. Berthelot gave 11·8 Cals. at 18° for the heat of vaporization of the solid trioxide. A. W. Porter calculated for the heat of vaporization 9·00 Cals. at 90°; 9·36 Cals. at 40°; 9·60 Cals. at 20°; and 9·71 Cals. at 0° for the liquid trioxide. Subtracting the interpolated value for the liquid at 18° from M. Berthelot's value for the solid, furnishes 2·2 Cals. per mol for the **heat of fusion;** H. Giran gave 1·9 Cals. A. Smits and P. Schoenmaker gave 1·8 Cals. for the mol. latent heat of fusion of the α-trioxide; and 2·9 Cals. for the β-trioxide; and 6·2 Cals. for the γ-trioxide; and H. Giran gave 9·49 cals. per gram for the liquid trioxide, and 11·39 Cals. for the solid trioxide. A. Smits and P. Schoenmaker gave 10·1 Cals. for the mol. latent heat of vaporization; 11·9 Cals. for the mol. heat of sublimation α-trioxide; 13·0 Cals. for that of β-trioxide; and 16·3 Cals. for γ-trioxide. A. Berthoud found that **Trouton's constant,** 32·5, is abnormal; and H. Giran said that the value for Trouton's constant points to a commencement of polymerization during liquefaction. A. Berthoud found that the constant, *f*, in the formula $\log (p_c/p)=f(T_cT^{-1}-1)$ falls irregularly from 3·66 at 34° to 3·29 at 180°, indicating that the molecules of the liquid are associated; the constant *f* in $\log (p_1/p_2)=f(T_1T_2^{-1}-1)$ is near 7·41 at 24° and corresponds with a mol. association which decreases rapidly with rise of temp. The **J. D. van der Waals' constant** $a=0·01629$, and $b=0·002684$. At the critical temp., the molecule is nearly normal, with association absent.

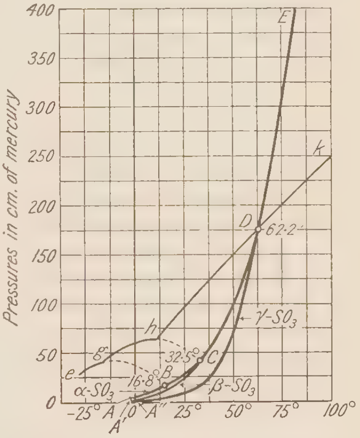


Fig. 76.—The Vapour Pressure Curves of Sulphur Trioxide.

J. Thomsen gave for the **heat of formation,** $(S,3O)=103·23$ Cals.; and $(SO_2,O)=32·16$ Cals.; H. Hess gave $(SO_2,O)=22·6$ Cals. M. Berthelot gave $(S,3O)=103·6$ Cals. for the liquid trioxide, 111·6 Cals. for the solid, and 149·4 for the aq. soln. J. Thomsen said that on mixing a mol of sulphur trioxide with an indefinitely large proportion of water, 38·88 Cals. of heat are developed; H. Hess said 40·4 Cals.; and M. Berthelot, 36 to 40 Cals. J. Thomsen gave $(SO_{3\text{liquid}},1000H_2O)=39·17$ Cals.; and M. Berthelot, $(SO_{3\text{gas}},H_2O,Aq.)=49·2$ Cals.; and $(SO_{3\text{solid}},H_2O_{\text{solid}})=19·8$ Cals.—*vide infra,* sulphuric acid. He also found $(SO_2,O)=34·2$ Cals. for the solid trioxide and $(SO_2,O)=22·6$ Cals. for the gas. G. Bodländer and K. von Köppen calculated from the equilibrium constant, $(SO_2,O)=26·3$ Cals. at constant press. between 515° and 610°; 31·2 Cals. between 610° and 650°—but the results are probably affected by some error. M. Bodenstein and R. Pohl calculated from the equilibrium constant $Q_p=22·8$ Cals. between 528°

and 680° ; 22·7 Cals. between 627° and 789° ; and 22·6 Cals. between 727° and 897°. The heat of soln. is discussed in connection with sulphuric acid—*vide infra.* R. Lucas calculated for the **free energy,** $18,840-11{\cdot}1T+2{\cdot}292 \log K_p$.

According to R. Nasini, the **index of refraction** of the α-trioxide at 20° for the red hydrogen line, H_α, is 1·4077 ; for the green hydrogen line, H_β, 1·41484 ; and for the yellow sodium line, 1·40965. The refractory power calculated from the μ-formula is 0·21053, and from the μ^2-formula, 0·12731. The **molecular refraction** for the H_α-line and the μ-formula is 16·48, and with the μ^2-formula, 10·18. C. Cuthbertson and E. P. Metcalfe gave 1·00737 for the index of refraction of the vapour of sulphur trioxide for light of wave-length $\lambda=0{\cdot}589\mu$. The additive value is 1·000960. R. Robl observed no fluorescence occurs in ultra-violet light.

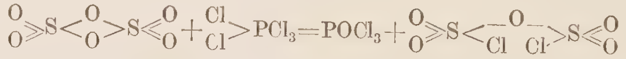
G. Magnus, and L. Bleekrode found that the **electrical conductivity** of the α-trioxide is very small. A. Geuther showed that liquid sulphur trioxide is not decomposed by the electric current, but if dissolved in conc. sulphuric acid, oxygen is given off at the anode, and a blue soln. of sulphur is formed at the cathode. P. Walden said that liquid sulphur trioxide has no ionizing power as a solvent. H. Schlundt gave 3·64 for the **dielectric constant** at 19°. P. Pascal gave $-0{\cdot}30\times10^{-6}$ for the **magnetic susceptibility** of the trioxide at 19°.

The α- and β-modifications of sulphur trioxide exhibit in general the same chemical behaviour, although, as G. Oddo[7] has shown, the β-form is not so active as the α-form. In many cases, sulphur trioxide acts as a strong oxidizing agent, and is at the same time reduced to sulphur dioxide. According to M. Berthelot, when a mixture of sulphur trioxide and **oxygen** is exposed to the silent discharge, sulphur heptoxide is formed. F. C. Vogel showed that sulphur trioxide unites vigorously with **water,** often explosively with the evolution of light and heat. When immersed in water, the trioxide hisses like red-hot iron, and a mixture of 4 parts of the trioxide and one of water is completely vaporized and light is emitted at the same time. In **air,** sulphur trioxide gives white fumes because the vapour of the trioxide unites with the water vapour, forming sulphuric acid. P. Schützenberger obtained red needles of *tetranhydrosulphatochlorine monoxide,* $(SO_3)_4Cl_2O$, by the action of **chlorine monoxide** on sulphur trioxide—*vide infra.* According to R. Weber, and A. C. Schultz-Sellack, a series of anhydrosulphates are formed by the action of **iodine** on sulphur trioxide—*vide infra.* R. Knietsch, H. Kämmerer, and R. Weber found that sulphur trioxide unites with dry **iodine pentoxide**—*vide infra,* sulphur oxyhalides. According to A. W. Williamson, **hydrogen chloride** acts on sulphur trioxide, forming chlorosulphonic acid ; while H. E. Armstrong, A. Michaelis, and F. Clausnizer observed that **hydrobromic acid** and **hydriodic acid** are oxidized respectively to bromine and iodine. H. Rose found that sulphur trioxide is absorbed by **alkali chlorides,** and A. Ditte observed that when heated with sodium chloride, chlorine and sulphur dichloropentoxide are formed. A. C. Schultz-Sellack added that the metal **fluorides, chlorides, bromides,** and **iodides** absorb sulphur trioxide—forming, in the last two cases, some bromine and iodine respectively. Complex salts are formed with sodium chloride, potassium chloride, silver chloride, and barium chloride. When these compounds are heated, sulphur trioxide is evolved, then some chlorine and sulphur dioxide, while the sulphate remains behind. W. Traube also obtained a complex with ammonium chloride—*vide infra,* the chloropyrosulphonates.

According to R. Weber, sulphur trioxide unites with **sulphur** to form blue sulphur hemitrioxide ; and A. C. Schultz-Sellack said that some sulphur dioxide is formed. P. Borinsky also studied this reaction. A. Geuther found that many **metal sulphides**—*e.g.* those of the alkalies, lead, and antimony—are oxidized by sulphur trioxide, forming a sulphate and sulphur dioxide, or a blue soln. of sulphur ; while the sulphides of iron and copper are not attacked. The observations of F. C. Vogel, G. F. Wach, H. Rose, N. W. Fischer, etc., on blue sulphur have been previously discussed. H. Rose found that **sulphur monochloride,** at 0°, absorbs the vapour of sulphur trioxide, forming $S_2Cl_2.5SO_3$—*sulphur pentanhydro-*

sulphatochloride. H. Rose showed that sulphur trioxide absorbs **sulphur dioxide** when both compounds are thoroughly dried by calcium chloride, and cooled to 0°, forming a complex approximating to **sulphur dioxydianhydrosulphate,** $2SO_3.SO_2$. When the liquid product is exposed to air, it evaporates rapidly, forming a thick cloud with the odour of sulphur dioxide, and leaving behind a trace of sulphuric acid. When kept a long time it loses part of its sulphur dioxide; it reacts violently with water, giving off sulphur dioxide; and it absorbs ammonia gas, forming a yellow product. A. C. Schultz-Sellack, and G. Karl observed that H. Rose's complex is only a mixture, for liquid sulphur di- and trioxides are miscible in all proportions; if an excess of sulphur dioxide be present, nothing separates out on cooling, but a mixture of equal parts deposits the β-trioxide which redissolves at ordinary temp. This mixture boils at 5°. If an excess of sulphur trioxide be present, the liquid may solidify at ordinary temp. When sulphur trioxide is treated with **sulphites,** sulphates and sulphur dioxide are formed; and, added A. C. Schultz-Sellack, no thiosulphate is formed. H. O. Schulze reported that the α-trioxide unites very energetically with **sulphuric acid** to form pyrosulphuric acid, and that with the β-trioxide the action is less energetic. R. Weber found that when sulphur trioxide and **potassium sulphate** are together heated in a sealed tube at 110°, two liquids are formed. The upper one is free sulphur trioxide, and the lower one, when cooled, forms **potassium heptanhydridosulphatosulphate,** $K_2SO_4.7SO_3$. Similar results are obtained with the **sulphates of ammonium, rubidium, cæsium, and thallium,** but not with the **sulphates of sodium, lithium, and silver.** W. Traube said that the persulphates form what he called perpyrosulphates (*q.v.*). According to R. Weber, P. Borinsky, and A. C. Schultz-Sellack, sulphur trioxide reacts with **selenium,** forming green selenium anhydrosulphate, $SeSO_3$, and with **tellurium,** to form red tellurium anhydrosulphate, $TeSO_3$; and with **selenium dioxide** there is formed selenium dioxyanhydrosulphate, $SO_3.SeO_2$; and **tellurium dioxide** forms **tellurium anhydrosulphatotetroxide,** $SO_3.2TeO_2$, studied by K. Vrba, J. J. Berzelius, G. Magnus, and D. Klein and J. Morel.

E. Berglund found that sulphur trioxide reacts with dry **ammonia,** forming imido- and amido-sulphonic acids (*q.v.*). According to F. Ephraim and H. Piotrowsky, sulphur trioxide is immediately reduced to sulphur hemitrioxide by **hydrazine.** A. Michaelis and O. Schumann, R. Weber, A. Brüning, and F. de la Provostaye described a complex $(SO_3)_2N_2O_3$, formed by the action of sulphur trioxide on **nitric oxide** or of sulphur dioxide on nitrogen peroxide. G. Karl also prepared the complexes $5SO_3.2N_2O_3$, boiling at 302°–305°, and melting at 198°–200°; and $6SO_3.3N_2O_3$, boiling at 360° and melting at 217°–230°. W. Manchot obtained the complex *sulphur heminitrosyl trioxide,* $2SO_3.NO$, by the action of sulphur trioxide on nitric oxide at 60°. It darkens and softens at 180°; melts at 215°–220°; and boils at 275° and 715 mm. It is readily decomposed by water into sulphuric acid and nitric oxide; it does not react with a soln. of ferrous or cupric sulphate in sulphuric acid; it is decomposed by heat into sulphur dioxide and nitrogen peroxide, and at 200°–300° it may be prepared from these gases. A. Brüning observed that with **nitrogen peroxide,** sulphur dioxide and crystals of **nitroxyl sulphur trioxide,** $SO_3.NO_2$ are formed. G. Oddo and A. Casalino observed that with nitrogen peroxide, the complex $O(SO_2.O.NO)_2$ is formed. R. Weber also obtained nitroxyl sulphur trioxide, which when heated forms **sulphur nitroxyl heptoxide,** $S_2O_7.NO_2$. With **nitric acid,** R. Weber said that the complex **nitrogen hydrotetrasulphatopentoxide,** $SO_3.N_2O_5.(H_2SO_4)_3$, or else $N_2O_5(SO_3)_4.H_2O$, is formed. It was also described by G. Karl; it boils at 218°–220°, and melts at 124°–125°. A. C. Schultz-Sellack observed that with **potassium nitrite** and liquid sulphur trioxide, **potassium nitrosylsulphate,** $K(NO)SO_4$, is formed. W. Traube said that with **sodium nitrate,** sodium nitroxyltrisulphonate (*q.v.*) is formed. R. Weber observed that with **nitrosyl chloride,** there is formed the complex **nitrosyl chloroanhydrosulphate,** $NOCl.SO_3$. F. C. Vogel showed that **phosphorus** soon takes fire in the vapour of sulphur trioxide and there is formed a crust of sulphur. H. Rose found that when **phosphine** is passed over sulphur trioxide at ordinary temp., sulphur dioxide and phosphorus pentoxide are formed, while G. Aimé added that yellow fumes are evolved which condense as a yellow powder, and next day a blue soln. of sulphur in sulphur trioxide is formed. R. H. Adie observed that phosphorus reacts with liquid sulphur trioxide, forming sulphur dioxide and **phosphorus ditritanhydrosulphatotetroxide,** $3P_2O_4.2SO_3$. R. Weber, and R. H. Adie made some observations on the complexes formed with **phosphorus pentoxide**—*vide* **8.** 50, 40. R. H. Adie observed that with well-cooled **phosphorous acid,** sulphur trioxide forms sulphur dioxide and a complex salt of **trianhydrosulphatophosphoric acid,** $H_3PO_4.3SO_3$. According to A. W. Williamson, and H. Schiff, **phosphorus pentachloride** reacts with sulphur trioxide, forming sulphuryl chloride, but A. Michaelis did not agree. G. Oddo and A. Sconzo represented the reaction : $SO_3+PCl_5=SO_2+Cl_2+POCl_3$; and with $(SO_3)_2$, by



$$\begin{smallmatrix}\mathrm{O}\\\mathrm{O}\end{smallmatrix}\!\geqslant\mathrm{S}<\begin{smallmatrix}\mathrm{O}\\\mathrm{O}\end{smallmatrix}>\mathrm{S}\leqslant\begin{smallmatrix}\mathrm{O}\\\mathrm{O}\end{smallmatrix}+\begin{smallmatrix}\mathrm{Cl}\\\mathrm{Cl}\end{smallmatrix}>\mathrm{PCl_3}=\mathrm{POCl_3}+\begin{smallmatrix}\mathrm{O}\\\mathrm{O}\end{smallmatrix}\!\geqslant\mathrm{S}<\begin{smallmatrix}-\mathrm{O}-\\\mathrm{Cl}\quad\mathrm{Cl}\end{smallmatrix}>\mathrm{S}\leqslant\begin{smallmatrix}\mathrm{O}\\\mathrm{O}\end{smallmatrix}$$

Sulphur trioxide oxidizes **phosphorus trichloride** to phosphoryl chloride. Sulphur trioxide (α- and β-) forms isomorphous mixtures with **phosphoryl chloride.** G. Oddo and A. Casalino studied the products of distillation of various mixtures and obtained distillates of intermediate composition. The f.p. curve, Fig. 77, has eutectics at —22° with 14·9 per cent. of SO_3, and at —41·4° with 33 per cent. There is a maximum at —16·62° corresponding with the formation of $SO_3.2POCl_3$, **diphosphoryl anhydrosulphato-hexachloride.** They used it as a cryoscopic solvent for mol. wt. determinations of SO_2Cl_2, CrO_2Cl_2, $POCl_3SO_3$, $(SO_3)_2$, etc. B. Kosmann, F. Reich, R. Weber, R. H. Adie, and A. Stavenhagen made some observations on the complexes formed with **arsenic trioxides**—*vide* **8.** 51, 37. These complexes include $As_2O_3.SO_3$; $As_2O_3.2SO_3$; $As_2O_3.3SO_3$; $As_2O_3.4SO_3$; $As_2O_3.6SO_3$; and $As_2O_3.8SO_3$; while R. Brandes, E. Péligot, J. A. Arfvedson, C. A. Schultz-Sellack, W. P. Dexter, and R. H. Adie obtained analogous complexes with **antimony trioxide** excepting $Sb_2O_3.6SO_2$. The complexes with **bismuth oxide** are usually regarded as basic sulphates. These complexes were studied by T. Poleck, A. Bon, A. Ditte, J. J. Berzelius and P. Lagerhjelm, A. C. Schultz-Sellack, C. Hensgen, and W. Heintz. The complexes with **vanadium pentoxide,** or the basic sulphates, were studied by J. J. Berzelius, L. Münzig, B. W. Gerland, J. Fritzsche, A. Ditte, and W. Prandtl ; those of **columbium pentoxide,** by H. Rose ; and those of **tantalum pentoxide,** by R. Hermann.

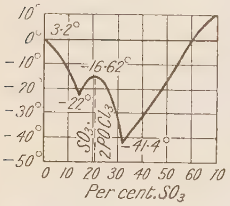


FIG. 77.—Freezing-point Curve of the System : SO_3–$POCl_3$.

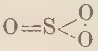
R. F. d'Arcy, A. C. Schultz-Sellack, G. Karl, A. Mertz, M. Levi and L. F. Gilbert, A. Géléznoff, and G. Gustavson made observations on the complexes formed with **boron trioxide**—*vide* **4.** 32, 26. G. Gustavson represented the reaction with **boron trichloride:** $2BCl_3+4SO_3=3SO_2Cl_2+B_2O_3.SO_3$, and with **boron tribromide,** bromine, sulphur dioxide, and the complex $B_2O_3.SO_3$ were formed. H. E. Armstrong represented the reaction with **carbon disulphide,** $SO_3+CS_2=S+SO_2+COS$. P. Schützenberger, H. E. Armstrong, and R. Gerstl discussed the reaction with **carbon tetrachloride :** $CCl_4+2SO_3=COCl_2+S_2O_5Cl_2$. G. Oddo and A. Sconzo found that the reaction is unimolecular, with the velocity constant, $k=0·0001447$, and therefore in accord with the assumption that an intermediate complex is first formed: $SO_3+CCl_4=Cl–SO_2–O.CCl_3$, followed by $Cl.SO_2.OCCl_3+SO_3=Cl.SO_2.O.SO_2.Cl+COCl_3$; or else the intermediate compound is $Cl.SO_2.O.CCl_2.O.SO_2.Cl=COCl_2+Cl.SO_2.O.SO_2.Cl$. A. C. Schultz-Sellack found that **mercuric cyanide** is decomposed by sulphur trioxide. A. W. Hofmann and G. B. Buckton, P. Eitner, B. von Barth and C. Senhofer, A. Pinner and F. Klein,

F. Gumpert, F. Krafft, A. Engelhardt, etc., studied the action of sulphur dioxide on **nitriles.** G. Karl discussed numerous mixed anhydrides of sulphur trioxide and organic anhydrides. H. N. Beilby noticed that sulphur trioxide attacks **glass** in the proximity of heated platinum. P. Hautefeuille and P. Margottet, K. Hüttner, and C. Friedel and A. Ladenburg studied complexes with **silica ;** A. Mertz, M. Blondel and H. Rose, complexes with **titania ;** P. Hautefeuille and J. Margottet, complexes with **zirconia ;** J. M. van Bemmelen, complexes with **germania ;** and R. Laurence, and J. V. Kraskowitz, complexes with **stannic oxide.**

According to G. Oddo, and H. B. Baker, dry sulphur trioxide does not attack the dried **metals** or the **metal oxides ;** B. Bizio also reported that, at ordinary temp., the vapour of the trioxide does not act on copper, silver, zinc, mercury, tin, lead, or iron. F. C. Vogel showed that warm mercury is attacked by sulphur trioxide, forming sulphur dioxide and mercuric sulphate ; and A. d'Heureuse, that at a red-heat, zinc or iron forms the metal sulphide and oxide ; C. Brückner observed that with red-hot magnesium powder, analogous products are obtained. I. Walz showed that sodium or zinc amalgam, in the presence of some water, forms hydrogen, then hydrogen sulphide, and then a mixture of hydrogen sulphide, and sulphur dioxide, and finally sulphur dioxide ; there is also a separation of sulphur.

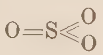
The trioxide is sent from the manufacturer in sealed drums of tinned iron. F. C. Vogel said that the trioxide can be held between the dry fingers, but it soon produces a penetrating sensation. Burns with the liquid trioxide, or the trioxide that is beginning to liquefy with absorbed moisture, are instantaneous on contact with the skin ; and the burns frequently become septic and are slow to heal. The trioxide is very poisonous and corrosive. It rapidly chars wood, paper, and many organic bodies. The dry trioxide does not redden dry litmus paper.

E. Drechsel[8] regarded the sulphur in sulphur trioxide as sexivalent corresponding with $(SO_2)O$; and H. Schröder considered that the vol. contraction attending the formation of the trioxide agreed more with a quadrivalent sulphur atom, and he wrote the formula :



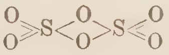
$$\mathrm{O{=}S}<\begin{matrix}\mathrm{O}\\\mathrm{O}\end{matrix}$$

This is also in harmony with the views of E. Divers. W. Odling and F. A. Abel found that sulphur trioxide is formed by the reaction : $SO_2Br_2+Ag_2SO_4=2AgBr+SO_2SO_4$, and hence regarded the trioxide as *sulphuryl sulphate*, SO_2SO_4. N. M. Teplow deduced from his vortex theory that the formula is S_4O_{12} or $(SO_3)_4$. G. Oddo supposed that the α-trioxide has the mol. wt. SO_3, and the β-trioxide $(SO_3)_2$, and gave for the graphic formulæ :



$$\mathrm{O{=}S}\ll\begin{matrix}\mathrm{O}\\\mathrm{O}\end{matrix}$$

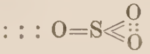
α-SO_3



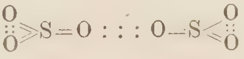
$$\begin{matrix}\mathrm{O}\\\mathrm{O}\end{matrix}\gg\mathrm{S}<\begin{matrix}\mathrm{O}\\\mathrm{O}\end{matrix}>\mathrm{S}\ll\begin{matrix}\mathrm{O}\\\mathrm{O}\end{matrix}$$

β-SO_3

so that the polymerized trioxide is a kind of sulphuryl sulphate, $(SO_2)SO_4$. J. A. N. Friend modified these formulæ in accord with the theory of latent valencies (dotted lines) :

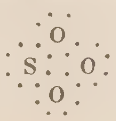


$$:::\mathrm{O{=}S}\ll\begin{matrix}\mathrm{O}\\\vdots\\\mathrm{O}\end{matrix}$$

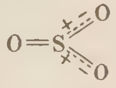


$$\begin{matrix}\mathrm{O}\\\vdots\\\mathrm{O}\end{matrix}\gg\mathrm{S{=}O}:::\mathrm{O{-}S}\ll\begin{matrix}\mathrm{O}\\\vdots\\\mathrm{O}\end{matrix}$$

I. Smedley also modified the graphic formula in accord with a quadrivalent oxygen and a sexivalent sulphur atom. W. Krings, and J. R. Syrkin discussed the electronic structure of sulphur trioxide, and E. B. R. Prideaux represented the molecule :



or



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§ 28. The Hydrates of Sulphur Trioxide and Sulphuric Acid

The so-called *oleum, Nordhausen sulphuric acid,* or **fuming sulphuric acid,** can be regarded as a soln. of sulphur trioxide or of pyrosulphuric acid in water. This product was probably one of the earliest forms of sulphuric acid produced for sale. It was made in Bohemia in early times, and during the Thirty Years' War the industry was transferred to Braunlage and Goslar, in the Harz country. The acid was distributed from the stores at Nordhäusen, from which place the acid took its name. Near the end of the eighteenth century the Bohemian factories were revived. At this time, the acid was made by the dry distillation of ferric sulphate—*Vitriolstein*—which, along with alum, had been made from slates containing pyrites since the sixteenth century. The retorts, holding nearly a kilogram of vitriol stone, were arranged in galleys, and the receivers fitted on as the thick fumes of sulphur trioxide appeared. The receivers contained some water or sulphuric acid. The operation was repeated until the liquid in the receivers had attained the desired concentration. The ferric oxide remaining in the retorts was ground and sold for use as a pigment under the names : *colcothar, caput mortuum, Venetian red,* or *English red.* The process was discussed by R. W. Hill,[1] E. V. Jahn, F. Stolba, and R. Schuberth—*vide supra,* sulphur trioxide. The yield of fuming acid is poor because the temp. of dissociation of ferric sulphate is so high that a large proportion of the sulphur trioxide is decomposed at the same time. The dissociation press. of the trioxide from ferric sulphate was found by G. Keppeler and J. d'Ans to be only 15 mm. at 640°, so that the temp. of the retorts must be much higher than this. They represented the effect of temp., T, on the press., p, of the trioxide : $Fe_2(SO_3)_3 \rightleftharpoons Fe_2O_3 + 3SO_2$, between 500° and 700°, by $\log p = 11{\cdot}8626 - 9755{\cdot}67T^{-1}$.

P. G. Prelier proposed to heat the alkali or alkaline earth sulphates with sulphuric acid to form the hydrosulphate, and to distil the water from the hydrosulphate, and the fuming acid or sulphur trioxide from the pyrosulphate. R. W. Wallace proposed a modification of this process ; and W. Wolters said that the liberation of sulphur trioxide from the pyrosulphate occurs at a lower temp. if some magnesium sulphate be present. This means that less sulphur trioxide is dissociated. W. Wolters also proposed to heat the pyrosulphate with anhydrous sulphuric acid, so as to distil off the sulphur trioxide: $Na_2S_2O_7 + H_2SO_4 = 2NaHSO_4 + SO_3$. A. M. Léon proposed to electrolyze monohydrated sulphuric acid so that the water decomposes into hydrogen and oxygen, and the resulting sulphur trioxide dissolved in the electrolyte to form the fuming acid. Fuming sulphuric acid is now made by the contact process whereby the resulting sulphur trioxide (*q.v.*) is dissolved in sulphuric acid of sp. gr. approximating $98\frac{1}{3}$ per cent. H_2SO_4, because, according to R. Knietsch, this acid contains neither free water nor free sulphur trioxide. O. Sackur showed that if free water be present, the α-SO_3 is not transformed to β-SO_3—*vide infra.*

Quite a number of hydrates of sulphur trioxide have been reported. The *hemihydrate,* $2SO_3.H_2O$, is the so-called **pyrosulphuric acid,** $H_2S_2O_7$—*vide infra* ; and the *monohydrate,* $SO_3.H_2O$, is the so-called **sulphuric acid,** H_2SO_4—*vide infra.* A. C. Schultz-Sellack[2] could not prepare a crystalline hydrate containing more sulphur trioxide than pyrosulphuric acid ; nor is there any evidence of the formation of such a compound on the f.p. curve, Fig. 78.

Nevertheless, R. Weber thought that he had obtained a *tetritahydrate*, $4SO_3.H_2O$, by adding sulphuric acid to sulphur trioxide. He said that it crystallized at 8° to 10°, and had a sp. gr. of 1·983. Again, V. A. Jacquelain reported prismatic crystals of the *tritetritahydrate*, $4SO_3.3H_2O$, to be formed by passing sulphur trioxide into conc. sulphuric acid; and H. W. F. Wackenroder, by cooling fuming sulphuric acid to −10°. The former said that the crystals melt at 26°, the latter at 10°.

J. C. G. de Marignac made some observations on the f.p. of fuming sulphuric acid *oleum;* and R. Knietsch gave the results shown in Table VI. The data in brackets represent freshly prepared soln., and the sulphur trioxide has not aged by the passage of α-SO_3 to β-SO_3. J. C. G. de Marignac said that crystals of H_2SO_4 separate from the conc. acid at 0·5°, and V. A. Jacquelain added that the conc. acid freezes at 0°, but it may be undercooled to −35° to −40°. H. Davy said that dil. sulphuric acid freezes at −25°, and T. Thomson, at −36° when confined in the bulb of a thermometer.

TABLE VI.—MELTING POINTS OF MIXTURES OF SULPHUR TRIOXIDE AND SULPHURIC ACID.

Free SO_3 per cent.	M.p.	Free SO_3 per cent.	M.p.	Free SO_3 per cent.	M.p.
0	10·0°	35	26·0°	70	9·0°
5	3·5°	40	33·8°	75	17·2°
10	−4·8°	45	34·8°	80	22·0°
15	−11·2°	50	28·5°	85	33·0° (27°)
20	−11·0°	55	18·4°	90	34·0° (27·7°)
25	−0·6°	60	0·7°	95	36·0° (26°)
30	15·2°	65	0·8°	100	40·0 (17·7°)

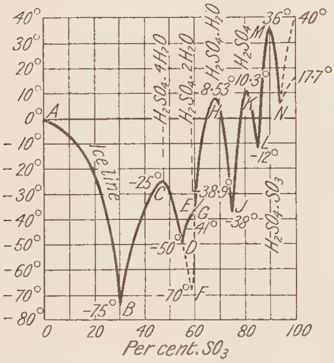


FIG. 78.—Freezing-point Curves of the System: SO_3–H_2O.

The so-called **monohydrated sulphuric acid,** $H_2SO_4.H_2O$, or the *dihydrate* of sulphur trioxide, $SO_3.2H_2O$, was said by V. A. Jacquelain to freeze at 8°, but, in a sealed tube, it can be undercooled to −35° to −40°. J. Dalton, and J. I. Pierre and E. Puchot, gave 7·5° for the f.p.; H. W. F. Wackenroder, 4°; L. Pfaundler and E. Schnegg, 8·81°; G. Lunge, 8°; D. P. Konowaloff, 8·55°; and R. Pictet, and J. Thilo, 3·5°. W. Hillmayr could not bring the f.p. of sulphuric acid to 4° by the addition of water. J. C. G. de Marignac gave 8·5° for the m.p. of this hydrate; H. W. F. Wackenroder, R. S. Tjaden-Moddermann, S. U. Pickering, and R. Lespieau, 8·53°; and J. I. Pierre and E. Puchot, 7·5. W. P. Jorissen said that crystals of the monohydrate are obtained by rapidly cooling 83·3 to 84 per cent. H_2SO_4 with ice; and A. D. Donk, by cooling with ice a mixture of 84 to 85 per cent. H_2SO_4 and barium or lead sulphate. Observations were also made by C. D. Carpenter and A. Lehrman. J. Thilo gave −39·9 for the f.p. of the *trihydrate* of sulphur trioxide, $SO_3.3H_2O$, or **dihydrated sulphuric acid;** R. Pictet, and E. von Biron gave −38·9°. C. D. Carpenter and A. Lehrman obtained analogous results for this metastable phase. S. U. Pickering reported a *pentahydrate* of sulphur trioxide, $SO_3.5H_2O$, or **tetrahydrated sulphuric acid,** $H_2SO_4.4H_2O$, melting at −25°, but the m.p. is rapidly lowered to −70° if a little water be present. E. von Biron gave −69° for the f.p. so that undercooling occurred. The results for the equilibrium diagram are compiled in Fig. 78. L. Pfaundler and E. Schnegg, S. U. Pickering, J. Thilo, and F. Rüdorff investigated the ice-line, *AB*, Fig. 78, and found:

SO_3 .	13·25	19·50	23·25	25·50	27·25	28·75	30·00	31·00
F.p. .	−10°	−20°	−30°	−40°	−50°	−60°	−70°	−75°

S. U. Pickering gave for the region of stability of tetrahydrated sulphuric acid, *BCD*, Fig. 78:

SO_3 .	31·75	33·75	36·00	39·00	43·25	**47·06**	49·75	55·50
F.p. .	−70°	−60°	−50°	−40°	−30°	**−25°**	−30°	−50°

so that the m.p. of the tetrahydrate is −25°. E. von Biron studied the region of stability of dihydrated sulphuric acid, *DEG*, Fig. 78; and J. Thilo, the metastable system where the dihydrate is not formed:

	Stable.				Metastable.			
SO_3 .	**56·00**	**59·69**	60·50	61·00	57·75°	59·75°	60·00	60·50
F.p. .	**−45°**	**−38·9°**	−40°	−41°	−60°	−70°	−60°	−50°

Hence, the m.p. of the dihydrate is −38·9°. L. Pfaundler and E. Schnegg, S. U. Pickering, M. Altschul, J. Thilo, and E. Knietsch's results for the region of stability of monohydrated sulphuric acid, *GHJ*, Fig. 78, are:

SO_3 .	61·00	62·50	63·50	65·50	**68·98**	72·00	74·75	76·00
F.p. .	−41°	−20°	−10°	0	**8·53°**	0°	−20°	−38°

where the m.p. of the monohydrate is S. U. Pickering's value; L. Pfaundler and E. Schnegg gave 8·81°. For the region of stability of sulphuric acid, *JKL*, Fig. 78, L. Pfaundler and E. Schnegg, S. U. Pickering, J. Thilo, E. Knietsch, and J. C. G. de Marignac gave:

SO_3 .	76·50	78·50	81·00	**81·62**	82·00	83·25	84·50	85·00
F.p. .	−30°	−10°	10°	**10·35°**	10	0°	−10°	−12°

where S. U. Pickering's value for the m.p. of sulphuric acid is 10·35°; J. Thilo's and J. C. G. de Marignac's, 10·5°; G. Oddo and E. Scandola's, 10·43°; A. Hantzsch's, 10·46°; J. N. Brönsted's, 10·49°; D. M. Lichty's, 10·43° to 10·45°; and R. Knietsch's, 10°. R. Knietsch determined values for the region of stability of pyrosulphuric acid, *LMN*, Fig. 78, and found:

SO_3 .	85·25	86·00	87·50	88·50	**89·89**	90·50	91·50	93·00
F.p. .	−10°	0°	20°	30°	**36°**	30°	20°	6·5°

where the m.p. of the pyrosulphuric acid is 36°. The subsequent progress of the curve, for soln. of sulphuric acid in sulphur trioxide, is doubtful. According to R. Knietsch, the curve bifurcates after rising from the minimum. One branch, referring to the freshly prepared soln. in α-trioxide, has the co-ordinates 26° for an acid of 95 per cent. of free SO_3 and 17·7° for 100 per cent. SO_3; the other branch, referring to a soln. in which the trioxide has had time to change to β-SO_3, has the co-ordinates 36° for 95 per cent. of free SO_3, and 40° for 100 per cent. SO_3.

There are singularities in the curves representing other physical properties of sulphuric acid—*vide infra*—corresponding with definite hydrates. There is room for doubting if the hydrates other than H_2SO_4, and even of pyrosulphuric acid itself, exist in the liquid state. J. Thomsen concluded from his thermochemical observations, and W. H. Perkin from his magnetic rotation observations, that sulphuric acid soln. contain the monohydrate; while M. Berthelot's thermochemical observations led him to conclude that still higher hydrates are present. L. Pfaundler and E. Schnegg's cryoscopic observations led them to believe that in conc. sulphuric acid, both the mono- and di-hydrates are present; and R. Lespieau, that the monohydrate is present; while S. U. Pickering, and R. Pictet postulated a large number of hydrates as a result of his observations on the f.p. of the soln.

Assuming that the amount of a hydrate formed in a soln. is proportional to its concentration, the rate of change of, say, the sp. gr. S with the change of concentration C will be a linear function of C, so that dS/dC will be represented by a straight line, say, $dS/dC=a+bC$. On treating the observed sp. gr. in this way, D. I. Mendeléeff found that dS/dC was discontinuous, so that when dS/dC and C were plotted, isolated lines were obtained each of which was supposed to represent a zone in which the corresponding hydrates—$H_2SO_4.H_2O$, $H_2SO_4.2H_2O$, $H_2SO_4.6H_2O$, and $H_2SO_4.150H_2O$—exist in soln. The mathematical argument is that if the *SC*-curve is really discontinuous, it will differentiate into a series of different curves each of which will represent the rate of change of the physical property *S* with the amount of the hypothetical hydrate in the soln. at that concentration. A change in the direction of the curve leads to a breaking up of the first differential coefficient into two curves which do not meet. S. U. Pickering applied the argument in the treatment of a number of determinations of the physical properties of soln. H. Crompton extended the argument to the second differential coefficient of the electrical conductivities of sulphuric acid soln. He inferred the existence of $2H_2SO_4.SO_3$, and $H_2SO_4.SO_3$, in the liquid. This subject was discussed by S. Arrhenius, J. Domke and W. Bein, J. N. Brönsted, H. E. Armstrong, J. Kendall and co-workers, E. H. Hayes, A. W. Rücker, O. J. Lodge, S. Lupton, and T. M. Lowry. It must be remembered that the *SC*- curve is purely empirical, and that the differentiation of experimental results very often furnishes quantities of the same order of magnitude as the experimental errors themselves. This is a very serious objection. S. U. Pickering has tried to eliminate the experimental errors, to some extent, by differentiating the results obtained by smoothing the curve obtained by plotting the experimental results. On the face of it this smoothing of experimental results is a dangerous operation even in the hands of the most experienced workers. Indeed, it is supposed that that prince of experimenters, H. V. Regnault, overlooked an important phenomenon in applying this very smoothing process to his observations on the vap. press. of sat. steam. In the words of O. J. Lodge :

> No juggling with feeble empirical expressions, and no appeal to the mysteries of elementary mathematics, can legitimately make experimental results any more really discontinuous than they themselves are able to declare themselves to be when properly plotted.

L. Schneider's sp. gr. determination led him to infer the existence of two hydrates, *viz.* $H_2SO_4.H_2O$, and $H_2SO_4.2H_2O$. E. Bourgoin studied the electrolysis of sulphuric acid and inferred that the dihydrate, $H_2SO_4.2H_2O$, or $S(OH)_6$, is present when the conc. of the acid ranges from $H_2SO_4.H_2O$ to $H_2SO_4.250H_2O$. T. Graham, from the capillary transpiration of sulphuric acid soln., inferred the presence of $H_2SO_4.H_2O$; R. Engel, from solubility determination, the existence of $H_2SO_4.12H_2O$. The observations by C. Fréry, G. Tammann, C. Dieterici, A. Ponsot, H. C. Jones, W. Ramsay and J. Shields, C. E. Linebarger, A. E. Dunstan and R. W. Wilson, S. U. Pickering, and V. S. M. van der Willigen on the optical and other properties of the acid, also led them to the hypothesis that definite but unstable hydrates are present in soln. If a mixture follows the mixture law—**1.** 10, 17—it is assumed that no chemical action has taken place between the constituents, and that the mol. state of the constituents is not changed by the mixing. Most binary mixtures deviate from the rule, and the results may be due to one or both these phenomena. E. W. Washburn concluded that in the property-composition curves the supposed points of discontinuity are due to experimental errors ; and that methods of studying hydration depending on the deviation of any physical property from the law of mixtures are incapable of yielding any conclusive information regarding the complexity or even the existence of hydrates in aq. soln. On the other hand, A. E. Dunstan and F. B. Thole said that the existence of definite maxima or minima on the property-composition curve, are indicated by almost every variety of physical property, and cannot be well denied. The minor changes of curvature which led S. U. Pickering to infer the existence of 22 different hydrates from his examination of the sp. gr., heats of soln., conductivity, vol. change on mixing and thermal expansion of sulphuric acid soln., may have a real existence, or they may be denied altogether, as was done by E. W. Washburn, or attributed to erroneous methods of plotting, as was done by H. Hartley and co-workers. Again, R. B. Denison showed that a maximum or minimum in the property-composition curve must be taken as giving a possible indication of the formation of a chemical compound, although there is no certainty. A sagged curve, without maxima or minima, may be caused by the dissociation of one of the constituents, or by their chemical combination, but a process involving an increased association of one of the constituents, as a result of their mixing, is unlikely. He also concluded that the curve representing the composition and the deviations from the mixture law gives a better indication of interaction between the constituents of mixed liquids. He added :

> The magnitude of the deviation from the mixture law is proportional when the conc. of the new substance attains a maximum value ; and further, when this is true, the mixture as a whole has the same fractional composition as the new substance formed. Although temperature changes may affect the form of the property-composition curve, especially as regards the maximum point, the point of maximum deviation from the mixture law is independent of temperature change.

J. L. R. Morgan and C. E. Davis applied this method to the available data dealing with aq. soln. of sulphuric acid, and found that evidence of the existence of the hydrate $H_2SO_4 : H_2O = 1 : 1$ was given by the sp. gr., compressibility, viscosity, and index of refraction curves ; of the 1 : 2-hydrate, by the index of refraction curves ; of the 1 : 3-hydrate, by the surface tension curves ; of the 3 : 1-hydrate, by the electrical conductivity, and viscosity curves ; of the 1 : 12-hydrate, by the electrical conductivity, and sp. gr. curves ; and of the 4 : 1- or the 5 : 1-hydrate, by the viscosity curves—*vide infra*, Figs. 82, 84, 85, 87, 88, 93, and 96.

W. Ostwald observed no evidence of the presence of hydrates in his work on the mol. conductivity of the acid ; while J. Domke and J. Bein said that the existence of hydrates cannot be deduced from sp. gr. determinations alone ; nor do the f.p. curves show the existence of the mono-, di-, tetra-, and hexahydrates, yet the hypothesis that hydrates exist in soln. is considered to be in accord with facts. B. C. Burt also showed that the vap. press. curves do not give any evidence of the formation of definite hydrates ; they do show that molecular complexes are formed. A. Smits and co-workers studied this subject. H. C. Jones compared the lowering of the f.p. of acetic acid by mixtures of sulphuric acid and water with the results with sulphuric acid and water alone. The results indicate the existence of the two hydrates, $H_2SO_4.H_2O$ and $H_2SO_4.2H_2O$, in acetic acid soln., but not the existence of any hydrates containing a larger quantity of water, even when as much as 37 eq. of water are present to one of sulphuric acid. These hydrates are somewhat unstable in the acetic acid when their soln. are very dil., and when the excess of water present is not very great. They can be regarded as dissociated under these conditions by the acetic acid into sulphuric acid and water. H. C. Jones and F. H. Getman, and H. C. Jones and H. P. Bassett calculated, from the sp. gr., the electrical conductivity and the f.p. of soln. containing M-mols of H_2SO_4 per litre, that in dil. soln., no water is held in combination, but with from $0{\cdot}5N$- to $5{\cdot}0N$-soln., the amount of combined water increases with the conc. of the soln. Assuming that m-mols of water are in combination with the acid per litre, and H mols of water are in combination with a mol of H_2SO_4 at the given conc. if a litre of soln. at that concentration contained 1000 grms. of water. H. C. Jones and co-workers found :

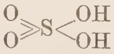
M .	0·60	1·00	1·50	2·00	2·50	2·73	3·28	4·37	5·0
m .	1·96	3·86	13·7	20·75	25·42	29·88	34·28	40·79	43·95
H .	3·3	3·9	9·2	10·4	10·2	10·6	10·4	9·4	8·6

A. Zaitschek studied the action of sulphuric acid on ethyl alcohol, and found that the equilibrium values did not give a satisfactory value for the constant K if the sulphuric acid be calculated as H_2SO_4 in the equation: $C_2H_5OH + H_2SO_4 \rightleftharpoons C_2H_5.HSO_4 + H_2O$, but if calculated as $H_2SO_4.2H_2O$, K is constant: $H_6SO_6 + C_2H_5OH \rightleftharpoons C_2H_5HSO_4 + 3H_2O$.

The constitution of the sulphuric acid.—About 1850, A. W. Williamson[3] represented sulphuric acid as a derivative of water:

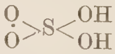
$$\underbrace{\mathrm{H}\quad\mathrm{H}}_{\mathrm{O}}\,\underbrace{\mathrm{H}\quad\mathrm{H}}_{\mathrm{O}}\qquad\qquad\underbrace{\mathrm{H}\quad\mathrm{SO_2}}_{\mathrm{O}}\!\!\underbrace{\quad\mathrm{H}}_{\mathrm{O}}$$

in consequence of its relation to chlorosulphonic acid, SO_3HCl, and sulphuryl chloride, SO_2Cl_2. With the advent of E. Frankland's structural formulæ, sulphuric acid was said "to contain two hydroxyl groups," meaning that in certain reactions, the OH-groups can be exchanged for eq. radicles; that there are certain relations between this acid and all other acids containing OH-groups; etc. C. Schorlemmer has said that the structural formula shows "the past and future of a compound," that is, "the relation subsisting between its progenitors and its progeny." The formula for sulphuric acid is expressed $SO_2(OH)_2$ for the following reasons: (1) Chlorine can react with conc. sulphuric acid, forming chlorosulphonic acid $ClHSO_3$, where one OH-group in sulphuric acid is replaced by chlorine. Phosphorus pentachloride, PCl_5, can displace one or two OH-groups in sulphuric acid, forming in the one case chlorosulphonic acid, $(HO)ClSO_2$, and in the other sulphuryl chloride $ClSO_2Cl$. Both these chloro-compounds react with water, forming sulphuric acid. The two OH-groups can be displaced together or separately, and we infer, from the rule of the constancy of structural arrangement that sulphuric acid, H_2SO_4, contains two hydroxyl or OH-groups. J. Thomsen also showed that the thermochemical data agree with the assumption that the two hydrogen atoms are directly united with oxygen atoms. On the other hand, H. E. Armstrong and F. P. Worley held that the formation of sulphuric acid from sulphuryl chloride, SO_2Cl_2, is not necessarily a proof that the acid contains two hydroxyl groups because of the alternative hypothesis that the sulphuryl chloride is first resolved into sulphurous acid and chlorine: $SO_2Cl_2+H_2O=SO_3H_2+Cl_2$, and that these products, *in statu nascendi*, interact with water to form sulphuric and hydrochloric acids: $SO_3H_2+H_2O+Cl_2=SO_4H_2+2HCl$. Similarly, the formation of chlorosulphonic acid is not necessarily a proof that an OH-group is present in sulphuric acid because the phosphorus pentachloride may merely dehydrate the acid: $SO_4H_2+PCl_5=SO_3+POCl_3+2HCl$. (2) Unlike sulphurous acid, it is possible to make but one compound, $CH_3O.SO_2.OK$, by replacing the hydrogen of the hydroxyl-groups with the radicle CH_3. Hence, it is inferred that the hydroxyl groups are related to the remainder of the atoms in the molecule H_2SO_4 in a symmetrical manner. This is not in agreement with I. I. Kanonnikoff's assumption that sulphur is quadrivalent, and that the formula is $(HO)_3.S.O.OH$. (3) Certain univalent hydrocarbon radicles—CH_3, C_2H_5, C_6H_5, etc.—can replace the chlorine in $ClHSO_4$ and in SO_2Cl_2 to form, say, phenyl sulphonic acid—$C_6H_5.SO_2.OH$, and diphenylsulphone—$(C_6H_5)_2SO_2$, respectively. The same compounds can be made by the oxidation of mercaptan, $C_6H_5.SH$, and of diphenyl sulphide, $(C_6H_5)_2S$, in which the radicle must be joined directly to the sulphur atom. Assuming that the radicles remain fixed to the sulphur atom during the oxidation, it is inferred that the hydroxyl groups in sulphuric acid, H_2SO_4, are directly attached to the sulphur atom. Hence, the formula $HO.SO_2.OH$ is preferable to $HO.O.S.O.OH$ for sulphuric acid. (4) We have not yet discussed whether the SO_2-group is constituted



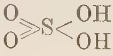
$$\begin{matrix}O\\O\end{matrix}\!\!\geqslant\!S\!<\!\!\begin{matrix}OH\\OH\end{matrix}$$

or



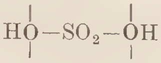
$$\begin{matrix}O\\ \cdot\\O\end{matrix}\!\!>\!S\!<\!\!\begin{matrix}OH\\OH\end{matrix}$$

The possible sexivalency of sulphur in sulphur hexafluoride, SF_6, points to the sexivalency of the sulphur atom in the sulphates, and hence it is probable that each of the two oxygen atoms is attached to the sulphur atom by a double valency. For these reasons, in agreement with E. Drechsel, the constitutional formula of sulphuric acid is written:



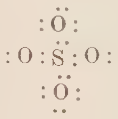
$$\begin{matrix}O\\O\end{matrix}\!\!\geqslant\!S\!<\!\!\begin{matrix}OH\\OH\end{matrix}$$

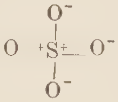
Remembering, of course, that it is very probable that the best of our structural formulæ is not so closely related to the actual orientation of the atoms in the molecule as the stuffed and dried specimens of a museum are related to the living organisms. P. Pascal found this formula agreed with his magnetic observations. A. E. Dunstan and R. W. Wilson added that each hydroxyl group is the seat of a very considerable residual affinity, as is evidenced by the formation of hydrates, of $H_2SO_4.SO_3$, etc., and accordingly they write the formula



$$HO-SO_2-OH$$

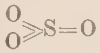
A. Hantzsch and F. Dürigen's observations on the refractive index agreed with the assumption that the constitution is either $[OS(OH)_3]^{\cdot}]SO_3OH]'$ or $[S(OH)_4]^{\cdot\cdot}[SO_2OH]_2''$—*sulphurylium sulphate.* The electrical structure has been discussed by H. Remy, K. Rolan, and H. Burgarth—*vide supra,* hyposulphurous acid. T. M. Lowry gave for the sulphate radicle, SO_4'',



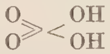


G. Oddo discussed the constitution in the light of his theory of mesohydry; and K. Rolan discussed the tetrahedral model of the sulphate ion. J. E. Marsh, and R. E. Hughes inferred that because anhydrous sulphuric acid, H_2SO_4, has no action on litmus, and does not form salts, it is really an anhydride.

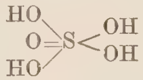
The three hydrates of sulphur trioxide—H_2SO_4; $H_2SO_4.H_2O$; and $H_2SO_4.2H_2O$ —are sometimes written graphically:



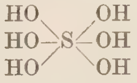
α-SO_3.



Metasulphuric acid, $(HO)_2SO_2$.



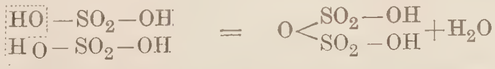
Parasulphuric acid, $(HO)_4SO$.



Orthosulphuric acid, $S(OH)_6$.

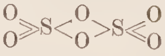
In harmony with the nomenclature applied to the periodic acids, the last formula represents the maximum hydroxide, corresponding with **orthosulphuric acid,** $S(OH)_6$, sulphur sexivalent, in agreement with T. Graham, the penultimate formula represents **parasulphuric acid,** $SO(OH)_4$; and the ordinary formula for sulphuric acid then represents **metasulphuric acid,** $SO_2(OH)_2$. There is not much experimental evidence in support of these formulæ, and the method does not help in dealing with the trihydrate, $H_2SO_4.3H_2O$; nor does it explain how the acids are usually dibasic. Hence, it is doubtful if this is the correct interpretation of the constitution of the hydrated forms of sulphuric acid. H. B. Kosmann regarded the monohydrate as a monobasic acid; and for the dihydrate he gave $S(OH)_6$.

With **pyrosulphuric acid,** or **disulphuric acid,** $H_2S_2O_7$, or $H_2SO_4.SO_3$, two molecules of sulphuric acid appear to be condensed into one mol. of disulphuric acid with the elimination of one mol. of water: $2H_2SO_4=H_2O+H_2S_2O_7$; or



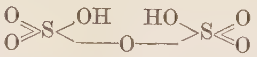
$$\begin{matrix}\boxed{HO}-SO_2-OH\\ \boxed{H\,}O-SO_2-OH\end{matrix} \;=\; O{<}\begin{matrix}SO_2-OH\\ SO_2-OH\end{matrix}+H_2O$$

on the assumption that the formula for sulphuric acid is $SO_2(OH)_2$; that disulphuric or pyrosulphuric acid is formed by the abstraction of a mol. of water from two mols. of sulphuric acid; and that when an anhydride is formed by the abstraction of water from a molecule of acid, each molecule of water abstracted from the acid, one oxygen atom takes the place previously occupied by two hydroxyl groups. The salts are dibasic. The bivalent acid radicle is S_2O_7. The relation between pyrosulphuric acid, β-sulphur trioxide, and sulphuric acid is illustrated by the formulæ :



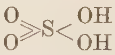
$$\begin{matrix}O\\O\end{matrix}\geqslant S<\begin{matrix}O\\O\end{matrix}>S\leqslant\begin{matrix}O\\O\end{matrix}$$

β-SO_3.



$$\begin{matrix}O\\O\end{matrix}\geqslant S<\begin{matrix}OH\\ \hline O\end{matrix}\begin{matrix}HO\\ \hline \end{matrix}>S\leqslant\begin{matrix}O\\O\end{matrix}$$

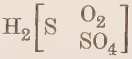
Pyrosulphuric acid.



$$\begin{matrix}O\\O\end{matrix}\geqslant S<\begin{matrix}OH\\OH\end{matrix}$$

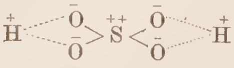
Sulphuric acid.

Hence β-sulphur trioxide can be regarded as the anhydride of pyrosulphuric acid ; and α-sulphur trioxide as the anhydride of sulphuric acid. A. Werner, and R. Schwarz have made some observations on the co-ordination theory ; and J. Meyer and V. Stateczny represented pyrosulphuric acid as an isopolyacid :



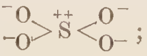
$$H_2\left[S\begin{matrix}O_2\\SO_4\end{matrix}\right]$$

but the co-ordination theory, as T. M. Lowry has pointed out, does not fit the facts so well as the ordinary theory, or the electronic theory :



$$\overset{+}{H}\cdots\begin{matrix}\bar{O}\\ \bar{O}\end{matrix}>\overset{++}{S}<\begin{matrix}\bar{O}\\ \bar{O}\end{matrix}\cdots\overset{+}{H}$$

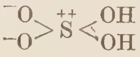
Electronic theory.



$$\begin{matrix}{}^{-}O\\ {}_{-}O\end{matrix}>\overset{++}{S}<\begin{matrix}O^{-}\\ O{-}\end{matrix}\ ;$$

Sulphate-ion.

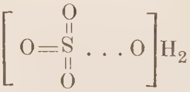
or



$$\begin{matrix}{}^{-}O\\ {}_{-}O\end{matrix}>\overset{++}{S}<\begin{matrix}OH\\OH\end{matrix}$$

Sulphuric acid.

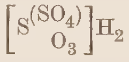
This subject was also discussed by N. V. Sidgwick. In the formula



$$\left[O{=}\overset{\overset{\textstyle O}{\|}}{\underset{\underset{\textstyle O}{\|}}{S}}\ .\ .\ .\ O\right]H_2$$

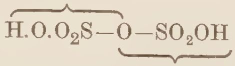
Co-ordination theory.

it is assumed that three of the oxygen atoms in the molecule are held by pairs of principal valencies while the fourth oxygen atom is held by a single auxiliary valency. This difference is not justified, and even A. Werner said that there is no real difference between principal and auxiliary valencies in complex nuclei. R. Schwarz regards pyrosulphuric acid as a isopolyacid, and he represented it by the unsymmetrical formula on the co-ordination theory. T. M. Lowry said that there is nothing to justify this since the conventional formula expressed in terms of electrons is more in accord with the mode of formation and behaviour of the compound :



$$\left[S\begin{matrix}(SO_4)\\ O_3\end{matrix}\right]H_2$$

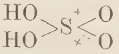
Co-ordination formula.



$$\overbrace{H.O.O_2S-O}\underbrace{-SO_2OH}$$

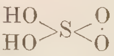
Conventional formula.

Here each sulphur atom is surrounded by four oxygen atoms satisfying the conditions for co-ordination although one oxygen must belong to both co-ordination spheres. J. Stieglitz discussed the polar structure of sulphuric acid, and E. B. R. Prideaux represented the electronic structure :



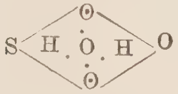
$$\begin{matrix}HO\\HO\end{matrix}>\overset{+}{\underset{\times}{S}}<\begin{matrix}O\\O\end{matrix}$$

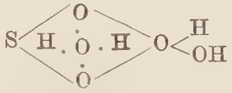
It might be added that E. Divers supposed that the sulphur in sulphuric acid is quadrivalent, and he wrote the formula :

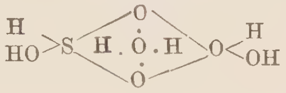


$$\begin{matrix}HO\\HO\end{matrix}>S<\begin{matrix}O\\ \dot{O}\end{matrix}$$

W. Spring preferred F. A. Kekulé's old chain formula HO.S.O.O.OH ; and W. A. Dixon, $S(O.OH)_2$. W. J. Pope and S. J. Peachey showed that sulphur can act as a tetrad ; and H. E. Armstrong and F. P. Worley say that there is no satisfactory evidence that sulphur ever has a higher valency. They account for the hexafluoride by the same argument that is generally applied to the polyhalides, namely, that the fluorine atoms form a closed system. W. Barlow and W. J. Pope's theory of valency volume indicates that the volume sphere of influence of sulphur, like that of oxygen, is never more than twice that of hydrogen ; and they therefore wrote the formula $SO_3.H_2O$ as advocated by J. J. Berzelius. H. E. Armstrong and F. P. Worley add that sulphur, like oxygen, whilst potentially a tetrad, usually behaves as a dyad. They based their formula for sulphuric acid on the hydrone theory (**1.** 9, 7), and regard the median oxygen atom as the centre of activity in the molecule of the acid. As a consequence of this hypothesis that sulphuric acid is a compound of sulphur trioxide with hydrone, it is assumed that sulphuric acid is really a monacidic compound like the sulphonic acids. They represented the monohydrate, $H_2SO_4.H_2O$, and the dihydrate in a similar way :


H_2SO_4


$H_2SO_4.H_2O$

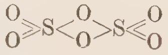

$H_2SO_4.2H_2O$

They add that the hydrate $H_2SO_4.4H_2O$ is perhaps formed by the union of $3H_2O$, *en bloc*, with the monohydrate. Some speculations on the constitution of the sulphuric acids were also made by N. M. Teploff, E. Wiberg, and A. Hantzsch and F. Dürigen.

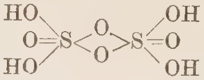
The analyses of H. Davy,[4] R. Chenevix, J. Dalton, M. H. Klaproth, C. L. Berthollet, and J. C. G. de Marignac are in agreement with the empirical formula H_2SO_4 ; the analyses of T. Graham, J. Thilo, R. Pictet, L. Pfaundler and E. Schnegg, with $H_2SO_4.H_2O$, and with $H_2SO_4.2H_2O$; and the analyses of S. U. Pickering, and E. von Biron, with $H_2SO_4.3H_2O$. The vapour density determination of H. St. C. Deville and L. Troost showed that the mols. of the vapour are dissociated : $H_2SO_4 \rightleftharpoons SO_3+H_2O$ at 440°, because the observed 1·74 agreed with the value 1·69 calculated for that change ; A. Bineau observed 2·155. The vapour density of H_2SO_4 which freezes at 10·43°, determined by V. Meyer's method in the vapour of anthracene (boiling at 351°) or triphenylmethane (boiling at 359°), gives a mol. wt. 100·9–101·9, so that at 10–20 above its b.p. sulphuric acid vapour is a mixture of $(H_2SO_4)_2.H_2SO_4$, SO_3, and H_2O molecules. Analogous results are obtained with sulphuric acid containing varying proportions of water.

Nitric acid has the mol. formula HNO_3, and the derivatives, N_2O_5, NO_2Cl, HNO_3, boil at 47°, 5°, and 86° respectively ; while the corresponding derivatives of sulphuric acid boil : sulphur trioxide at 46·2° ; sulphuryl chloride at 69·1° ; and sulphuric acid at 338°. The difference in the intervals between the b.p. of the acid and anhydride in the two cases is explained as an effect of the polymerization of sulphuric acid, and not of nitric acid. Hence, H. M. Vernon assumed that in conc. sulphuric acid the mols. are present as $(H_2SO_4)_2$ because of the relatively high b.p. ; and W. Vaubel also obtained a similar result for the complexity of the molecule at 338°. G. C. Longinescu, however, inferred that the molecule is not associated. The change in the mol. surface energy of sulphuric acid with temperature is so small that E. Aston and W. Ramsay considered the liquid contained highly polymerized molecules—probably $(H_2SO_4)_{23}$. The f.p. of soln. of sulphuric acid in acetic, chloracetic, and formic acids, and in nitrobenzene correspond with the doubled formula $(H_2SO_4)_2$. Methyl sulphate, $(CH_3)_2SO_4$, in absolute sulphuric acid (freezing at 10·43°), forms methyl trihydratosulphate, $CH_3H_3(SO_4)_2$, which is a salt of a **bis-sulphuric acid,** or **disulphuric acid,** $H_4(SO_4)_2$, while in acetic acid or benzene, the mol. wt. of methyl sulphate corresponds with the formula $(CH_3)_2SO_4$, which is a salt of metasulphuric acid, H_2SO_4. Hence, it is inferred that the formation of methyl trihydrosulphate does not depend upon the existence of a doubled mol. of methyl sulphate, but on a doubled sulphuric acid mol., $(H_2SO_4)_2$. G. Oddo and G. Anelli, therefore, infer that, like sulphur trioxide, sulphuric acid exists in two forms, the one disulphuric acid, $(H_4SO_4)_2$, is represented by ordinary absolute sulphuric acid ;

and that the metasulphuric acid, H_2SO_4, is not known in the free state. Disulphuric acid is also regarded as the second hydrate of β-sulphur trioxide :

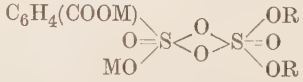


β-Sulphur trioxide.



Disulphuric acid.

pyrosulphuric acid, $H_2S_2O_7$, being the first hydrate. Hence, pyrosulphuric acid is **metadisulphuric acid,** $H_2S_2O_7$, and bis-sulphuric acid is **paradisulphuric acid,** $H_2S_2O_8$. A. Geuther explained the constitutional formula of some sulphonates—*e.g.* dialkyl disulphobenzoate,



where M and R denote respectively metal and alkyl radicle—on the assumption that they are derivatives of paradisulphuric acid. This view of the constitution is taken to explain the dimorphism and other variable properties exhibited by many sulphates. According to E. J. Maumené, the elevation of temp. which occurs when olive oil is mixed with sulphuric acid, is greater or less, according as the acid has been recently boiled or otherwise. Thus, with acid boiled a few hours previously, a temp. of 42° was obtained ; whereas with acid that had been kept about two months, only 34·5° was reached. No change in the optical or other physical properties of the acid revealed the existence of this structural modification. M. Berthelot also found that the heats of soln. of the freshly-prepared and long-kept acids are the same.

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§ 29. Sulphuric Acid—History, Occurrence, and Preparation

So far as our knowledge goes, the ancients were acquainted with only one acid, namely, vinegar or acetic acid; but G. F. Rodwell[1] thought it probable that sulphuric acid was known to them. Jabir Ibn Hayyan, in his *The Invention of Verity or Perfection*, an Arabian work supposed to have been written in the eighth century, refers to the production of *dissolving water* by distilling nitre with vitriol; and to the formation of a spirit by distilling alum. The twelfth-century translation of Geber's *De investigatione magisterii* refers to a spirit which can be expelled from alum by heat, and which possess solvent powers. According to F. Hoefer, Abou Bekr al Rhases, a tenth-century writer of Persian origin, referred, *en termes obscurs et ambigus*, to an oil which was obtained by the dry distillation of *atrament* or ferrous sulphate. The residue was *crocus ferri* or ferric oxide; the oil could have been no other than sulphuric acid. Indeed, the fuming acid has been manufactured by that very process. In the twelfth century, Albertus Magnus, in his *Compositum de compositis*, obtained what he called *spiritus vitreoli romani* by the dry distillation of Roman alum. He said: *Sulphur philosophorum* is not common sulphur, but rather the spirit of Roman vitriol; and it is obtained by the distillation of vitriol. In his *De rebus metallicis et mineralibus*, Albertus Magnus used the word vitriol for the first time for ferrous sulphate—*viride atramentum, quod a quibusdem vitreolum vocatur.* About the same time, Vincent de Beauvais, in his *Speculum naturali*, alluded to a *solutiva corporum* which was prepared in a similar manner, and which must have been sulphuric acid. Towards the end of the sixteenth century, A. Libavius referred to an acid as the *spiritus aluminosum*, and he showed that it is the same acid as *oleum vitrioli* obtained by the weathering of pyrites, and as *spiritus vitrioli per campanum* obtained by burning sulphur under a bell-jar. At the beginning of the seventeenth century, Augustus Sala described the preparation of *spiritus vitrioli* by the dry distillation of iron or copper vitriol, and by burning sulphur in moist vessels accessible to air. Shortly afterwards the preparation of the acid was also described by N. Lemery, E. R. Seehl, and by J. C. Bernhardt. The seventeenth-century pseudonymous writer Basil Valentine described the preparation of *olea vitrioli* by the dry distillation of a mixture of ferrous sulphate and sand, and of *oleum sulphuris* by burning sulphur with nitre, but he regarded these two acids as different substances—*vide supra*, sulphur trioxide. He said that by gradually heating copper and ferrous sulphates in a luted retort, there collects in the receiver first a white spirit which is *mercurius philosophorum*, and then a red spirit which is *sulphur philosophorum*. J. R. Glauber also refers to the preparation of corrosive oil of vitriol; and H. Cardan, to the oil obtained by distilling *chalcante* or *misy*—the former is supposed to be partially oxidized pyrites, and the latter, an ochre impregnated with copperas. J. Kunckel showed that the *mercurius philosophorus* or *spiritus vitrioli* differs from *sulphur philosophorum, oleum vitrioli*, or *ros vitrioli* only in being associated with different proportions of water. R. Boyle also said that the acids obtained from vitriol and from burning sulphur are identical. The properties of the acid were described by W. Gould, R. Boyle, H. Cavendish, H. Boerhaave, and C. J. Geoffroy.

The phlogistian's view that sulphuric acid is dephlogisticated sulphur has been discussed in connection with sulphur. The phlogistians regarded sulphuric acid as an elementary substance. This hypothesis seemed to be supported by R. Boyle's observation that sulphur is produced by heating sulphuric acid with turpentine; and by J. H. and C. J. Gravenhorst's observation that sulphur is produced when a vegetable decoction putrefies in the presence of sodium sulphate. R. Kirwan supposed that sulphur was phlogisticated sulphuric acid, and his analysis gave 59 per cent. of sulphuric acid, and 41 per cent. of phlogiston, although R. Boyle, and J. Mayow had previously stated that sulphur must be regarded as a constituent of sulphuric acid. In 1772, and 1777, A. L. Lavoisier showed that sulphuric acid is a hydrated oxide of sulphur, and its composition was established by the analyses of J. J. Berzelius, C. L. Berthollet, L. J. Thénard, R. Chenevix, J. B. Trommsdorff, J. B. Richter, C. F. Bucholz, M. H. Klaproth, H. Davy, and J. Dalton—*vide supra*, sulphur trioxide.

To-day, sulphuric acid is manufactured by oxidizing sulphur dioxide. This is effected in the so-called chamber process by using nitrogen oxide as a catalytic agent in the presence of steam; and in the so-called contact process by using finely divided platinum, or one of the metal oxides as catalytic agent—*vide supra*, sulphur trioxide. W. Ostwald[2] has pointed out that if *Zeit Geld ist*—time is money—then catalysis, which may be said to accelerate the speed of reactions without the expenditure of energy, is of the greatest importance in chemical industries because in speeding up reactions, the catalytic agent saves time and incidentally money. In the seventeenth century, sulphuric acid was usually manufactured *per campanum*—by the bell—for pharmaceutical purposes. Here, an earthenware dish with a charge of sulphur rested on an iron tripod in an earthenware pan, and a glass bell was suspended over the burning sulphur. The operation of burning was repeated until the acid was sufficiently concentrated to enable it to be satisfactorily concentrated in glass retorts. It was recommended to work during the equinoxes because the air then contained more moisture. Another improvement, recommended by K. Digby, was to put water in the pan so as to condense the fumes. J. R. Glauber, and N. Lemery improved the process by mixing about 5·5 per cent. of nitre with the sulphur. This hastens the oxidation of the sulphur dioxide to sulphur trioxide, and, added C. Neumann, it enables the sulphur to burn by itself without communication with the external air, and by this means, nearly all the fumes are preserved. It was said that the resulting acid does not contain any nitrous acid, because the acid of nitre is destroyed by the deflagration. This improvement was also patented in 1749 by J. Ward and J. White. According to R. Dossie, in 1740, J. Ward was manufacturing sulphuric acid at Richmond, near London, using large glass bell-jars up to 66 gallons capacity. The subsequent history of sulphuric acid manufacture has been described by G. Lunge, W. Wyld, O. Guttmann, J. Mactear, W. F. Reid, R. F. Carpenter, etc. They said that the manufacture was introduced into England by C. Drebbel; and that the introduction of lead chambers in place of glass bell-jars is due to Mr. Roebuck of Birmingham, who erected a leaden chamber about 6 ft. cube in 1746. Numerous other plants were soon afterwards erected in different parts of the country, and the number and capacity of the lead-chambers was increased so that in 1805, a factory at Burnt Island had 360 chambers each with a capacity of 192 cub. ft. P. de Wolf and E. L. Larison described the history of the manufacture of sulphuric acid in the United States. The process was improved by blowing steam into the chambers during the combustion of the sulphur; and in 1793, F. Clément and J. B. Désormes improved the process by feeding the chambers with a continuous supply of air. Between 1807 and 1810, according to J. Mactear, J. Holker made the process continuous by continuously burning the sulphur. J. L. Gay Lussac's tower for recovering the oxides of nitrogen escaping from the chamber gases was introduced about 1827 in a works at Chauny; and the concentrating and denitrating tower of J. Glover, about 1859, in a works near Durham.

The occurrence of sulphuric acid.—J. S. Eisholtz[3] concluded that air contains some sulphuric acid because colcothar—the residue from the dry distillation of ferrous sulphate—after exposure to air furnishes on dry distillation some acid; and G. E. Stahl, likewise, because potash-lye furnishes crystals of the alkali sulphate after it has been exposed to air for a long time. G. W. Wedel objected to J. S. Eisholtz's experiment, maintaining that the sulphuric acid had not all been driven from the colcothar, and that the effect was due to absorbed moisture; and G. E. Stahl's observation has not been confirmed. A. R. Smith found that the air of Manchester contained 3772 grms. H_2SO_4 per million cub. metres. G. H. Bailey investigated the air of Manchester and its suburbs; and H. Ost, the air in the neighbourhood of Hanover—*vide* **8.** 49, 1. Free sulphuric acid occurs in many volcanic spring waters; and J. D. Dana[4] called natural free sulphuric acid, *sulphatite.* A. von Humboldt, and J. B. J. D. Boussingault observed that the Rio Vinagre which flows from the Purace in the Andes contains 1·11 grms. sulphuric acid per litre. At the summit of Purace, the water contains hydrogen sulphide. B. Lewy found 0·255 per cent. of sulphuric acid in the water of a spring at Paramor de Ruiz, New Granada. The acid was found by A. Fleischer to occur in the spring-water of Porjaer Rudösberge in the Carpathians; T. S. Hunt, 3·5016 grms. per litre in the Sour Spring of Tuscarora, Canada; J. Lefort, 3·643 grms. per litre in the crater water of Popocatepetl, Mexico; W. J. Craw and H. Erni, 2·007 grms. per litre in the water of Oak Orchard, Alabama, New York; S. de Luca, 1·1730 grms. per litre in the water of the solfatara at Pozzuoli; F. Stolba, in the spring-water of Dobran, Claraschacht; E. Pollacci, in the spring-water of Aix, Savoy, and of San Filippo, Tuscany; G. Baldassani, in the grotto Zoccolino, Tuscany; J. P. de Tournefort, in a grotto at Milo; G. de Dolomieu, in a cave at Ætna; and J. W. Mallet found the free acid in drainage-wells west of the Neches river, Gulf of Mexico; and in the acidic waters of Louisiana no less than 5·290 grms. of free sulphuric acid per litre were present. According to A. H. van der Boon-Mesch, and C. G. C. Reinwardt, the water of the sulphuric acid lake of Java is white owing to the presence of precipitated sulphur, and the vapour of hydrogen sulphate escapes from the crater. As G. Bischof says, the sulphuric acid has not been formed in the volcanoes but near the surface where air has access—part of the hydrogen sulphide exhalation is oxidized to sulphur, and part to sulphuric acid—not sulphurous acid. A. E. Fersman observed that the opal hydrogel of the Daryasa Hill, Transcaspia, contains adsorbed sulphuric acid. Combined sulphuric acid in the form of sulphates is very common in natural waters, and is distributed as sulphates of the metals and ammonium in the organic and inorganic kingdom.

C. Bödeker and F. H. Troschel,[5] S. de Luca and P. Panceri, and R. L. Maly found up to 2·47 per cent. H_2SO_4 in the secretions of some molluscs; D. Gibertini, and R. Kayser found the free acid in wines; and A. Hilger, in acetic acid. G. Musso and F. Schmidt discussed the occurrence of sulphates in cow's milk; S. Grimaldi, and C. Papi, in whey; and P. B. Hawk and J. S. Chamberlain, in the excretions of man. According to R. Meyer-Bisch, the concentration of total sulphuric acid in the blood-serum of normal individuals is about 18 mg. per cent. This amount is altered to a variable extent in nephritis and constantly raised in diabetes. The sulphuric acid content of the cerebro-spinal fluid is greater than that of the serum, and is raised in meningitis, syphilis of the central nervous system, and encephalitis. Pleural exudates and œdema fluids contain about the same amount of sulphuric acid as the blood serum; lymph from the thoracic duct contains a variable amount but greater than the blood.

The formation of sulphuric acid.—Sulphuric acid is formed by dissolving sulphur trioxide in water, and D. M. Lichty[6] described a method of preparing sulphuric acid of definite concentration by mixing stoichiometrical proportions of these constituents. As indicated in connection with sulphur, sulphuric acid is slowly formed when the element is oxidized in moist air; by heating sulphur and water in a sealed tube at 200°; by the combustion of sulphur in moist air—W. C. Young, C. Heisch, and G. W. Wigner; by the electrolysis of water with sulphur electrodes—E. Becquerel, by the action of various oxidizing agents—chlorine, hydrochlorous acid, nitric acid, and a mixture of nitric acid and potassium chlorate—on sulphur. W. Wicke also noticed that a stick of sulphur wound about with lead wire gives crystals of lead when dipped in lead nitrate, and lead sulphate is formed; with copper wire and copper nitrate soln., copper sulphate and sulphide are formed. T. Parkman also noted the formation of sulphuric acid when sulphur is boiled with a soln. of lead acetate, silver nitrate, or a cupric salt. The formation of sulphuric acid by the oxidation of sulphur dioxide—by hydrogen dioxide, the halogens, hypochlorous acid, nitric acid, and by many salts of the metals, *e.g.* auric chloride, mercuric salts, manganese sulphate, etc.—has already been discussed. Commercial processes have been suggested for oxidizing sulphur dioxide with chlorine, and produce hydrochloric and sulphuric acids simultaneously: $SO_2+2H_2O+Cl_2=H_2SO_4+2HCl$—*e.g.* W. Haehner, H. Tobler, and A. Coppadoro. B. Neumann and F. Wilczewsky obtained sulphuric and hydrochloric acids from sulphurous acid and chlorine.

Sulphuric acid is formed by the action of oxidizing agents on the polythionic acids (*q.v.*) and on thiosulphuric acids or thiosulphates (*q.v.*). E. F. Smith obtained sulphuric acid as a product of the electroxidation of metal sulphides. Sulphuric acid was shown by O. Binder, U. Collan, A. Lieben, E. von Mayer, and E. Priwoznik to be a product of the combustion of coal gas; and S. D. Crenshaw, of the combustion of anthracite. E. Salkowsky, and W. J. Smith observed the formation of sulphuric acid in the organism—*vide supra*, sulphur. G. Guittonneau isolated from soils a micro-organism capable of transforming thiosulphates into sulphates.

L. Thompson[7] obtained an acid of the highest degree of purity by treating calcium sulphate with oxalic acid, and evaporating the filtrate; and C. L. Bloxam, by allowing sulphur dioxide—prepared from sodium sulphite and sulphuric acid at a low temp.—nitric oxide—from a mixture of potassium nitrate, ferrous sulphate, and sulphuric acid—and water to come in contact in a glass vessel as in the chamber process for sulphuric acid—*vide infra*. For other methods, *vide infra*, the purification of sulphuric acid by distillation, etc.

Other methods of making sulphuric acid have been proposed. For instance, H. W. Deacon[8] found that sulphur dioxide mixed with atm. air, and in the presence of a soln. of cupric sulphate, is oxidized to sulphuric acid. H. Rössler applied the process to acid smokes; and J. B. Daguin substituted salts of manganese, iron, or tin for cupric sulphate. A. M. G. Sébillot passed sulphur dioxide and air through heated columns of pumice-stone into which steam with more air was passed—*vide supra*, sulphur trioxide.

O. Bender[9] exposed a mixture of sulphur dioxide and oxygen, with or without nitrogen oxides, in an oxyhydrogen flame, or of water-gas. If air be present, a little nitric acid is formed. W. Hallock exposed the mixture to an ionizing agent—*e.g.* a radioactive material; H. Kühne, to ultra-violet rays of a mercury arc lamp; and A. Coehn and H. Becker, to ultra-violet rays, at a temp. above 300°—*vide supra*, sulphur dioxide.

Although H. Buff and A. W. Hofmann,[10] and H. St. C. Deville obtained sulphur trioxide by the action of an electric spark discharge on a mixture of sulphur dioxide and oxygen, A. F. C. Reynoso patented a process for making sulphur trioxide by sparking a compressed and cooled mixture of sulphur dioxide and atm. air. Various modifications—by L. Bradley, W. Garroway, W. J. Kee and U. Wedge, H. Riesenfeld, H. V. Welch, H. M. Weber, etc.—have been devised for dealing with burner gases, etc.

L. Wacker[11] proposed to prepare conc. sulphuric acid by the electrolysis of water or dil. sulphuric acid through which a continuous stream of sulphur dioxide is passed. Modifications were devised by L. P. Basset, C. F. Böhringer, G. C. de Briailles, A. Fischer and G. Delmarcel, A. Friedlander, A. von Grätzel, C. B. Jacobs, A. C. Johnson, P. G. Salom, etc. F. P. van Denberg electrolyzed molten calcium sulphate and subsequently hydrated the sulphur trioxide which was evolved. According to E. R. Watson, sulphuric acid and sodium hydroxide can be obtained by the electrolysis of a 40 per cent. aq. soln. of sodium sulphate, employing a platinum, iron, or copper cathode and a platinum, lead, or carbon anode, a current density of about 4 ampères per sq. dcm., and a potential difference between the electrodes of about 5 volts, starting the electrolysis at about 30° and allowing the temp. to rise to about 40°; conversion into sodium hydroxide and sulphuric acid can be effected with a current efficiency of about 90 per cent., and an energy efficiency of about 50 per cent. provided electrolysis is not carried beyond an average conversion of about 25 per cent. Nearly all the sodium sulphate may be crystallized out of the alkaline liquor, leaving sodium hydroxide in the mother-liquor nearly pure, and sodium hydrosulphate may be similarly obtained from the acid liquor. Sulphuric acid is best produced from the sodium hydrosulphate by distillation. The process was investigated by H. V. Atwell and T. Fuwa. According to R. Saxon, the electrolysis of a soln. of an equimolar mixture of copper sulphate and ammonium aluminium sulphate yields a soln. of sulphuric acid which may reach a conc. of 17 per cent. in 7 hrs. Simultaneously copper is deposited on the cathode and aluminium hydroxide in the catholyte.

The sulphates of the alkalies, alkaline earths, and lead are not appreciably affected, chemically, at a red-heat, but the hydrosulphates form pyrosulphates, which split up into the normal sulphates and sulphur trioxide; but while the reaction can be utilized for the manufacture of fuming sulphuric acid, the cost is too great for the ordinary acid. The ferric and aluminium sulphates and other acid sulphates yield sulphuric acid at a comparatively low temp., but the other sulphates, requiring a high temp. for their decomposition, yield sulphur dioxide and oxygen, and comparatively little sulphuric acid or sulphur trioxide. Most of the sulphates, too, require sulphuric acid for their preparation in the ordinary way; and the cost is too great except in the case of ferric sulphate for the manufacture of fuming acid, discussed by F. S. Wartman and H. E. Keyes,[12] and O. C. Ralston. The enormous stores of gypsum or anhydrite in nature have incited many to devise attempts to tap the contained sulphuric acid. For instance, a series of processes—by M. Kuenzi, E. Frémy, W. Townsend, C. von Grabowsky, E. V. Evans, H. A. Archereau, H. Hilbert, H. Trey, R. Wedekind, V. Cummings, etc.—are based on driving out the sulphur trioxide or sulphur dioxide and oxygen by heating gypsum with quartz, sand, clay, etc., with or without iron oxide or pyrites. O. Köhsel heated a mixture of finely ground gypsum and coal dust so as to form carbon dioxide and calcium sulphide. The carbon dioxide was passed over heated water and calcium sulphide from a previous operation so as to form calcium carbonate and hydrogen sulphide. The hydrogen sulphide was burnt for sulphur dioxide, which was then delivered into the lead-chambers and treated in the ordinary manner. O. Schott used a mixture of sodium sulphate, gypsum, and coal, and employed the resulting frit for glass making. A. Scheurer-Kestner, M. Martin, and J. Anzies heated calcium or magnesium sulphate with ferric oxide, with or without coal. B. Dirks prepared ammonium sulphate by the action of ammonia and carbon dioxide on gypsum; treated the ammonium sulphate with phosphoric acid, and decomposed the resulting ammonium phosphate by heat to recover the ammonia and phosphoric acid. W. Dominik, and I. Moscicki and W. Dominik discussed a modification of this process. Many processes have been devised[13] for obtaining sulphuric acid from alkali hydrosulphates—*e.g.* nitre-cake. E. R. Watson described a process for making sulphuric acid and sodium hydroxide by the electrolysis of sodium sulphate.

The chamber process of manufacture.—In the chamber process of making sulphuric acid,[14] there are involved:

1. *The burners.*—The sulphur dioxide is made in the burners, (1) by the combustion of sulphur (brimstone); (2) by heating pyrites, zinc blende, the spent oxide from gas-works, etc., in a current of air; or (3) by the combustion of hydrogen sulphide, etc.—*vide supra*, sulphur dioxide. Air is drawn through the burners in excess of that required for oxidizing the sulphur. The necessary draught is regulated by chimney, or fans. The burner gas contains sulphur dioxide, nitrogen, and oxygen.

2. *Nitrating the gas.*—For introducing nitrous fumes into the gas, a mixture of sodium nitrate and sulphuric acid is heated in the track of the hot burner gas, or nitric acid is introduced into the liquid which trickles down the Glover's tower; or nitrous fumes are introduced into the lead chambers.[15] S. F. Spangler discussed the use of ammonia-oxidation plants in place of the nitrate process; and R. Tern, the oxides derived from the oxidation of air.

3. *The Glover's tower.*—The hot mixture of air and sulphur dioxide passes up a

tower packed with flints, volcanic lava, or blue bricks, down which trickles a mixture of a weak acid from the lead chambers and the strong nitrated acid which has been used to absorb nitrous fumes, and recovered in the Gay Lussac's tower to be described later. The tower is lined with volvic lava, or blue bricks. The functions [16] of the Glover's tower are: (1) to recover the nitrous oxides from Gay Lussac's tower; (2) to cool the gases from the burners; (3) to help to concentrate the acid trickling down the tower; (4) partly to oxidize the sulphur dioxide from the burners; and (5) to introduce the necessary nitric acid into the lead chambers by running nitric acid down the tower along with the nitrated acid or nitrous vitriol from the Gay Lussac's tower. Before the acid reaches the foot of the tower it is fully or almost fully denitrated: $2(NO_2)HSO_3+SO_2+2H_2O=3H_2SO_4+2NO$.

4. *The lead reaction-chambers.*—The mixture of air, sulphur dioxide, and nitrous fumes passes into a set of three leaden chambers—may be a total capacity of 150,000 cubic feet—into which steam is blown from low press. boilers. The gases in the chambers are thus intimately mixed. The oxidation of the sulphur dioxide mainly occurs in the first two chambers. The gases are passed through the chambers slowly so as to allow time for all the sulphur dioxide to be oxidized. The third chamber serves mainly to dry the gases. The chambers are kept cool enough to condense the sulphuric acid which collects on the floor and is drawn off periodically. It is called **chamber acid.** Chamber acid contains between 62 and 70 per cent. H_2SO_4.

The cost of erecting and maintaining the leaden reaction chambers, and the large amount of space they occupy, have incited inventors to devise methods for reducing the capacity of the chambers, or for substituting less costly plant. The proposals for manufacturing sulphuric acid in a diminished space are based on the assumption that if the gases were better mixed the sulphur dioxide would be more quickly oxidized, and smaller chambers would be practicable. K. Abraham [17] studied the movements of the gases in the chambers. The better mixing of the gases can be effected by artificial draughts. T. Richters [18] proposed to mix the gases by introducing a steam injector which aspirated the gases from the lower part of the chamber and re-introduced them at the top. Various modifications of the idea have been proposed by N. P. Pratt, O. Guttmann, H. Rabe, A. J. Boult, F. Blau, J. A. Hart, O. Wentzki, Thomson-Houston Co., G. K. Davis, H. Porter, T. Meyer, E. Hartmann and F. Benker, etc. The mixing of the gases can be accelerated by the use of specially shaped chambers. Thus, in E. and T. Delplace's [19] annular chambers, the gases are continually changing their direction owing to the shape of the chambers. F. J. Falding used a very tall chamber trusting to convection currents to hasten the mixing. This system has been discussed by F. J. Falding and W. R. Cathcart, H. Petersen, E. Hartmann, G. Lunge, R. Hoffmann, etc. T. Meyer devised what he called tangential chambers arranged so that the entrance pipes form a tangent with the walls of the annular chambers. The gases circulate round and round before finding their exit from the centre. G. Lunge discussed this system. Modifications have been devised by C. W. Crosse-Legge, J. Harris and D. H. Thomas, H. V. Welch, R. E. Dior, S. Zeromsky, etc.

In another set of proposals for reducing the capacity of the chambers, the chamber gases are exposed to a greater surface to facilitate the condensation of the mist. J. Mactear [20] showed that a tray 1 sq. ft. area placed in a vitriol chamber collected 708 grms. of sulphuric acid in 24 hrs.; if 12 pieces of glass strips 12×6 in. were placed vertically in the tray, the amount of acid obtained rose to 1641 grms., and when the glass strips were placed horizontally, the amount of acid rose to 3226 grms. The idea of introducing glass sheets into the chambers was proposed by W. Ward; and various other materials were used by V. Brulfer, K. Walter and E. Boeing, L. G. Fromont, H. R. Dawson, etc.

Another way of increasing the production of acid is by the use of intermediate or reaction towers for mixing and cooling the gases between the chambers. This is illustrated by the towers discussed by J. Thyss,[21] E. Sorel, G. Lunge, P.W. Hofmann, H. H. Niedenführ, F. B. Hacker and P. S. Gilchrist, R. H. Winsloe and B. Hart, B. Hart and G. H. Bailey, W. Wyld and S. W. Shepherd, H. Rabe, etc. In the extreme case, the lead chambers are wholly replaced by towers or their equivalent. This is illustrated by J. Barbier,[22] F. Benker, F. Blau, A. Burkhardt, J. F. Carmichael and F. Guillaume, Chemische Fabrik Griesheim-Elektron, F. Curtius, A. G. Düron, Durand, Huguenin and Co., A. W. Fairlie, J. Fels, W. Fulda, P. S. Gilchrist, O. Guttmann, B. Hart and G. H. Bailey, E. Hartmann, R. Hasenclever, N. L. Heinz, N. L. Heinz and M. F. Chase, W. Hunt, E. W. Kauffmann, Kaltenbach Pipe Process, P. Kestner, N. Krantz, W. F. Lamoreaux, E. L. Larison, S. Littmann, A. MacDougal and H. Rawson, J. Mackenzie, T. Meyer, R. Moritz, O. Mühlhäuser, C. Opl, P. Parrish, H. Petersen, P. Pipereaut, H. Porter, K. B. Quinan, C. J. Reed, G. Schliebs, T. Schmiedel and H. Klencke, Steuber and Co., J. Thede, L. A. Thiele,

S. J. Tungay, H. Vollberg, W. H. Waggaman, K. Walter and E. Boenig, U. Wedge, O. Wentzki, etc.

5. *The Gay Lussac's tower.*—The excess air which leaves the lead chambers is highly charged with nitrogen oxides. These are recovered by causing the exit of gases from the chambers to pass up a tower, packed with coke, down which conc. sulphuric acid is trickling. G. Lunge,[23] and P. E. Hallwell showed that coke slowly reduces nitrous acid or nitroxylsulphonic acid to nitric oxide, and a packing made from glass, or vitrified bricks or stoneware of special shapes is in many cases preferred. The packing of gas scrubbing towers was discussed by S. J. Tungay, F. G. Donnan and I. Masson, and F. C. Zeisberg. The conc. acid absorbs the nitrous fumes, forming nitroxylsulphonic acid. Nitric oxide is not absorbed, but nitrous acid and nitrogen peroxide are absorbed.[24] The nitrated acid or nitrous vitriol which collects at the foot of the Gay Lussac's tower is pumped to the top of the Glover's tower along with some of the more dilute chamber acid. The nitrated acid trickling down the Glover's tower loses the absorbed nitrous fumes and some water. The acid which collects at the foot of the tower contains about 80 per cent. H_2SO_4.

6. *The concentration of the acid.*—The chamber acid is not allowed to attain a higher concentration than about 62 to 70 per cent. H_2SO_4, because a more conc. acid begins to absorb the nitrous fumes from the chambers. The chamber acid is therefore concentrated further either in the Glover's tower as indicated above, or in leaden concentrating pans until it contains about 79 per cent. of H_2SO_4. If the acid be much more conc. than this, it begins to attack the lead evaporating pans rather seriously. This acid is now called *B.O.V.* or *brown oil of vitriol*—its brown colour is due to the presence of organic matter. H. de Hemptinne [25] recommended concentrating the acid *in vacuo* at 200°–205° when lead is not perceptibly attacked. The further concentration of the brown oil of vitriol is effected either by boiling it in vessels or stills of glass, vitrified quartz, platinum, or acid-resisting alloys. The acid may also be placed in these stills direct from the chambers. At first, very weak sulphuric acid distils over. The conc. of the acid in the still gradually rises until it has about 98·3 per cent. H_2SO_4—*vide infra*, physical properties. Any further concentration cannot be done by evaporation since the acid itself then distils over. The further concentration of the acid, in the event of its being required, was effected by G. Lunge,[26] and H. Osterberger and E. Capella, by cooling the conc. acid, and crystals of 100 per cent. H_2SO_4 were obtained.

W. Strzoda concentrated sulphuric acid by first evaporating it in open lead pans to a sp. gr. 1·7; and then passing the acid downwards through vertical pipes externally heated. The vapours pass through a tower, where they are separated into an acid of sp. gr. 1·7 and steam. The acid passes back into concentrating pipes. The acid obtained in the process is 97 to 98 per cent. strength. Numerous observations [27] have been made on the concentration of sulphuric acid. P. Vaillant discussed the theory of the evaporation. The consumption of heat in the concentration of sulphuric acid has been discussed by L. Cerutty,[28] C. Tyler, P. S. Gilchrist F. C. Sutton, and F. C. Zeisberg. The general subject of the concentration of the acid is the subject of a work by J. W. Parkes. F. Tate discussed the merits of various systems of concentration in platinum vessels, in W. C. Heraeus's vessels of platinum plated with gold; in vessels of porcelain; and in vessels of iron, or enamelled iron. A. Scheurer-Kestner described the losses attending the use of platinum concentrating pans; and F. Lütz, the use of glass vessels. Electrical heating was discussed by A. H. Bucherer, and C. Häussermann and F. Niethammer.

The distillation of sulphuric acid is too costly an operation except for special purposes. As the quantity of acid in the retort diminishes, lead sulphate may separate from the liquid. The acid is particularly troublesome to boil because of that percussive ebullition called *bumping*. The acid appears quite tranquil for a little while, and as soon as a certain amount of heat has accumulated in it, a great volume of vapour is suddenly evolved, and acid may be projected violently into the receiver, and the retort broken. J. L. Gay Lussac said that platinum foil may counteract the violent bumping to some extent; A. Bobierre recommended platinum, and F. M. Raoult, hard gas carbon which is only slightly attacked by the boiling acid. J. J. Berzelius showed that the efficacy of the platinum ceases after a while; and he recommended applying the heat only to the sides of the retort, not to the bottom. According to J. Reese, this condition is obtained by resting the retort on a base of a bad conducting material—ashes, sand, etc. A. Müller used a ring burner. W. Dittmar recommended drawing a thin stream of air through the boiling acid.

Instead of using glass retorts, C. Negrier [29] used a series of porcelain dishes arranged so that the lip of one dish projects over the next dish. The dishes are placed in series and heated from below, while the acid to be concentrated runs from the highest to the lowest dish. This furnishes the *cascade system of concentration.* F. Benker improved the process by enclosing the dishes in a chamber of volvic lava so that the flue gases are kept separate from the acid vapours which are condensed in a lead-lined box filled with granular stoneware or silica. An acid containing 97–98 per cent. H_2SO_4 can be so obtained. The basins may be of vitreous silica, or one of the so-called acid-resisting alloys. The basins may be associated with leaden pans for the preliminary heating. Cast-iron dishes are also used for the concentration of acid from 94 to 98 per cent. H_2SO_4. The action is slight, and most of the iron separates from soln. as insoluble sulphate as the acid becomes highly conc.

The concentration of sulphuric acid by hot-air is displacing the cascade system. In *L. Kessler's hot-air process*,[30] the hot gases from a producer charged with coke are drawn over the surface of the acid by means of a steam exhaust. The acid is contained in a trough of volvic lava, and the vapour passes up a short tower down which dil. acid is trickling. The acid vapours are here partly absorbed, and the remainder is arrested by a lead-lined condenser filled with fragments of coke. T. C. Oliver, P. S. Gilchrist, and others have modified the plant. The concentration in *A. Gaillard's spraying process* [31] is effected by hot-air. The dil. acid is sprayed into the top of a cylindrical tower of volvic lava, the hot gases from a coke producer enter at the bottom of the tower. The hot gases passing away from the top of the tower are scrubbed in a chamber filled with fine coke to remove the acid vapours. The acid is in a conc. condition as it arrives at the bottom of the tower. The process was examined by J. W. Parkes and E. G. Coleman, A. Hutin, A. G. Duron, and G. Stolzenwald. M. Kaltenbach investigated the electrostatic precipitation of the mist from the spray concentration plant.

The purification of sulphuric acid.—Commercial chamber acid always contains a number of impurities derived partly from the raw materials—*e.g.* pyrites in the burners, the nitre, the lead of the chambers, etc. The impurities may be hydrochloric acid from the nitre (J. McMullen,[32] R. J. Kane, and J. F. W. Johnston), hydrofluoric acid (J. Nicklès), sulphur dioxide, selenium, nitrogen oxides—*e.g.* nitric oxide, and nitrous and nitric acid, alkalies from the nitre (J. F. A. Göttling), copper (J. J. Berzelius, and J. B. Trommsdorff), calcium and magnesium (C. H. Pfaff), zinc and mercury (J. J. Berzelius), aluminium, thallium (W. Crookes), titanium (C. H. Pfaff), tin (J. J. Berzelius), lead, arsenic, antimony, iron (E. Kauder), arsenic (J. J. Berzelius), and organic matter. A sample of ordinary commerical sulphuric acid of sp. gr. 1·7 was found [33] to contain in grams per litre:

As_2O_3	As_2O_5	HCl	N_2O_3	$FeSO_4$	$Al_2(SO_4)$	Cu, Zn, Pb, Se, Sb, Bi
3·18	2·56	0·08	0·52	0·56	0·46	traces

The impurities are usually present in proportions too small to be injurious for many of the uses to which the acid is applied; but there are cases where the impurities may cause trouble. Thus, B. Deutecon [34] found that a minute proportion of mercury may make the acid less suitable for pickling brass objects; nitric acid may cause wool to be stained in the carbonizing process, arsenic and chlorides render the acid unsuitable for storage batteries, and F. J. Falding showed that such an acid is unsuitable for preparing certain colours, and for pickling iron previous to galvanizing or tinning. Arsenic is also considered objectionable when the acid is to be used in the preparation of foodstuffs, and medicines. F. Schultz found that refined white petroleum becomes yellow when agitated with sulphuric acid containing a little selenium. E. Barruel showed that the sulphuric acid contaminated with nitrogen oxides may attack platinum, and particularly so if chlorides be present. The nitrogen oxides and arsenic are important enough to require very special attention. The brown colour of sulphuric acid is attributed to organic matter which is destroyed when the acid is further concentrated. R. Nörrenberg[35] alluded to a red colour produced by the contact of sulphuric acid, containing a little nitrous acid, with iron tanks. Selenium may colour sulphuric acid red or green as indicated below. The presence of lead sulphate, and of selenium, may also cause the acid to appear muddy, and ultimately form a sediment—F. von Giese.

According to G. Lunge and W. Abenius,[36] nitrogen compounds may be present as nitric oxide, and as nitroxylsulphonic, nitrous and nitric acids; and, according to J. Kolb, nitric acid can be present in acids with a lower conc. than sp. gr. 1·84. The detection of these compounds was discussed by E. Barruel, E. Desbassayns de Richemont, V. A. Jacquelain, E. Kopp, G. Lunge, A. Rose, H. Schiff, A. Vogel, H. W. F. Wackenroder, R. Warington, J. H. Wilson, and C. Wittstock. Most of the nitrogen compounds are expelled from sulphuric acid when the arsenic is removed by hydrogen sulphide. A. Kemp, and A. Payen described a method of treating the acid with sulphur dioxide to remove the nitrogen oxides; E. Barruel, and P. Schwarzenberg, by treating the heated acid with finely-divided sulphur, but F. Bode said that the process is not efficient; J. Löwe recommended oxalic acid; H. D. Steenbergen, agitation with mercury; H. W. F. Wackenroder, sugar; W. Skey, charcoal—only for the dil. acid; K. Rosenstand-Woldike, lead or barium dioxide; and J. Pelouze, ammonium sulphate. The ammonium sulphate treatment has proved the most satisfactory of reagents. The process was examined by J. Pattinson, W. F. Gintl, and G. Lunge and W. A. Abenius.

Sulphuric acid prepared from sulphur does not usually contain arsenic, and if arsenic be present, it is only in insignificant traces. Spent oxide from gas-works yields an acid with 40 to 50 parts of arsenic per million, while acid derived from blende, or pyrites, usually contains more arsenic. According to P. Parrish,[37] 30 per cent. of the arsenic in the pyrites will be found in the chamber and 20 per cent. in the unvolatilized cinders, and about 50 per cent. in the acid from Glover's tower. M. Stahl found that with Spanish pyrites, the acid from the first chamber contained 0·16 per cent. As_2O_3; from the second, 0·01 per cent.; from the third, 0·007 per cent.; and from the last, only a trace; while with pyrites from Virginia containing less arsenic, the acid from the first chamber had 0·005 per cent. As_2O_3; and acid from the other chambers, none. In some cases, where the gas from the burners passes through chambers for collecting dust, much of the arsenic is arrested as arsenical flue dust.[38] C. L. Bloxam found that all the samples of commercially pure acid which he examined contained traces of arsenic; acid purified by heating with sodium chloride, by distillation with potassium dichromate, and by partial electrolysis, all contained traces of arsenic. E. W. Martius,[39] H. W. F. Wackenroder, F. P. Dulk, H. D. A. Ficinus, J. B. L. Arthaud, A Vogel, F. Selmi, E. Seybel and H. Wikander, H. Hager, L. Rosenthaler, R. Kissling, G. Bressamin, etc., studied the occurrence of arsenic in sulphuric acid. According to E. E. Hjelt, the arsenic in the acid from Gay Lussac's tower contains nitrous vapours in soln., and these oxidize the arsenic to the pentoxide, whereas in Glover's tower the excess of sulphur dioxide converts the arsenic to the trioxide. The high-valent arsenic does not volatilize when the acid is distilled, whereas the low-valent arsenic is volatile. Hence, A. Bussy and H. Buignet, F. M. Lyte, M. Blondlot, and W. R. Hardwick oxidized the arsenic to the non-volatile, quinquevalent form by the addition of nitric acid. The acid can then be mixed with a little ammonium sulphate to destroy the nitrous acid, and then distilled. M. Blondlot said that an excess of ammonium sulphate reduces quinquevalent arsenic to the volatile, tervalent form. This A. Bussy and H. Buignet deny. F. M. Lyte destroyed the nitrogen compounds in the acid by heating it with oxalic acid to 110°, and adding potassium dichromate to the acid cooled to 100°. This oxidizes the arsenic, and the liquid yields arsenic-free sulphuric acid when distilled. Potassium permanganate can also be used as the oxidizing agent. M. Morancé tried to purify the acid by fractional freezing, but the separation of arsenic was not complete. R. S. Tjaden-Moddermann, and A. A. Hayes also proposed to purify the acid by freezing. E. Gothard recommended removing arsenic by shaking the acid with colzer oil so as to precipitate the arsenic, lead, etc., in the form of soaps.

Many have suggested removing the arsenic as volatile trichloride by heating the acid with hydrogen chloride—*e.g.* G. D. Beal and K. E. Sparks, above 125°—the b.p. of arsenic trichloride—and at a much lower temp. than the b.p. of the acid. Thus, L. A. Buchner first destroyed the nitrogen oxides with oxalic acid, then reduced the arsenic to the tervalent form by heating the acid with carbon, and then passed a current of hydrogen chloride through the liquid. A. Bussy and H. Buignet said that this process does not give a satisfactory result, but L. A. Buchner said that this only occurs when quinquevalent arsenic is not reduced to the tervalent form. J. Löwe heated the acid with sodium chloride, and H. Schwarz with a mixture of sodium chloride and charcoal dust. W. Tod added that a temp. of 130°–140° is sufficient when hydrogen chloride is used, and 180°–190° with sodium chloride. J. L. Smith said that neither process is sufficient to remove all the arsenic. N. Gräger used barium chloride ; F. Selmi, lead chloride ; G. Bressanin, hydriodic acid ; and H. Hager, chloroform. The United Alkali Co., and W. W. Crowther and co-workers have many patents for the removal of arsenic as volatile chloride. If selenium be absent, the arsenic can be reduced with sulphur or charcoal, and hydrochloric acid, and if selenium be present, sulphur is not advisable. W. Hasenbach, and the Verein Chemischer Fabriken, Mannheim, recommended extracting the arsenic trichloride with hydrocarbons, mineral oils, and glycerides ; the Chemische Fabrik Griesheim-Elektron, with benzene or its derivatives—*e.g.* dichlorobenzene—or with carbon tetrachloride or acetylene tetrachloride. If chamber acid is being treated, a little iodine or hydriodic acid and sulphur dioxide is recommended for reducing quinquevalent arsenic to the tervalent form. The removal of arsenic as sulphide was formerly used because impurities like lead, antimony, and selenium are removed at the same time, and sulphurous, nitrous, and nitric acids are destroyed. The precipitation of quinquevalent arsenic is much slower than is the case with tervalent arsenic. M. A. Kolontayeff recommended an electrolytic process. Calcium sulphide or alkali waste has been recommended as precipitant ; A. Dupasquier used barium sulphide ; J. L. Smith, ferrous sulphide ; J. L. Smith, and L. Ducher, alkali sulphides ; and G. Thomson, ammonium sulphide. W. Thorn, and R. Wagner recommended sodium or barium thiosulphate. Various modes of applying hydrogen sulphide for the purpose have been suggested by W. Hunt, K. Scheringa, G. E. Davis, A. A. Hayes, H. E. J. Cory, The United Alkali Co., I. F. J. Kupfferschläger, T. S. Moore, G. E. Clark, and R. Bithell and J. A. Beck. L. W. McCay heated the acid with the gas at 100° under press. G. Lockemann, and T. S. Moore studied the general subject of the dearsenification of sulphuric acid. Like arsenic, antimony is removed from sulphuric acid as sulphide ; similarly also with lead. When conc. sulphuric acid is diluted, a white turbidity of lead sulphate appears. The subject was examined by A. A. Hayes, G. C. Wittstein, P. A. Bolley, J. Löwenthal, etc. A. Dupasquier showed that conc. sulphuric acid containing lead does not give a precipitate with hydrogen sulphide. M. A. Miropoljskaja said that the mercury which is not removed from sulphuric acid by distillation, can be separated by electrolysis with a gold anode.

Selenium occurs in sulphur pyrites, and it may find its way in the flue-dust, in the chamber mud, and, as shown by G. E. Davis,[40] G. Lunge, and P. Kienlen, in sulphuric acid. This subject was discussed by J. Personne, J. G. Dragendorff, E. Schmidt, G. Lunge, A. Lamy, F. Schultz, A. Scheurer-Kestner, A. Jouve, N. A. Orloff, M. P. Sergéeff, L. Deutsch, F. Schlagdenhaufen and C. Pagel, etc. According to A. E. Drinkwater, selenium is present as selenium dioxide or as selenium ; S. Littmann said that, contrary to F. Winteler, he did not find selenic acid in the chambers ; it is formed only in the presence of the strongest oxidizing agents, and the conditions for its formation do not occur in the chambers under normal conditions. In the burner gas the excess of sulphur dioxide reduces the selenium dioxide to selenium. He said that the dark red sludge observed in the hot acid from Glover's tower contains 2–4 per cent. of the total selenium in the pyrites. Incompletely denitrated Glover's acid contained all its selenium in the form of selenium dioxide ; dil. samples of Glover's acid, on the other hand, contained a part of the selenium in some other form of combination in which it had the property of being precipitated from soln. as a red powder by merely diluting the acid ; in such cases the precipitation of red selenium on dilution could be prevented by drawing a feeble stream of nitric oxide through the acid immediately after it had been diluted. Inasmuch as only about 20 per cent. of the selenium from the pyrites can be accounted for in the Glover's tower, it follows that the major portion must pass on to the chambers. The tubes leading from the Glover's tower to the chambers contained both red selenium and the combined form, but no dioxide. The green colour of the ordinary commercial acid is due to the presence of the compound $SeSO_3$; when this acid is further conc. it becomes colourless owing to the conversion of this substance into the colourless SeO_2. Wherever nitrosylsulphuric acid is formed or decomposed, either of the various forms of selenium is converted into selenious acid ; and the main quantity of the selenium escaping from the pyrites exists in the form of a very volatile labile combination corresponding with a lower state of oxidation, such as SeO ; in this form it is readily reduced to elementary selenium or oxidized to selenium dioxide. J. Personne said that selenium can be removed by diluting the acid with three vols. of water, and precipitating with sulphur dioxide ; F. Schlagdenhaufen and C. Pagel rectified the acid by distillation from potassium dichromate ; and A. E. Drinkwater, by heating it with sodium chloride, when the selenium passes off with the hydrogen chloride.

P. Askenasy [41] purified sulphuric acid by electrolyzing the agitated liquid with lead electrodes at ordinary or a slightly elevated temp., with a current density of 1–2 amps. per sq. decimetre, and 6 volts. The ozone which is formed destroys organic substances and hydrochloric acid ; finely-divided sulphur reduces the nitrogen oxides ; and the hydrogen sulphide precipitates metals, etc.

The theory of the lead chambers.—The catalytic action of the nitrogen oxides on the oxidation of moist sulphur dioxide in the lead chambers has given rise to much discussion. F. Clément and J. B. Désormes [42] opened up the subject in 1795. All are agreed that the oxidation is not directly effected by oxygen ; but an intermediate compound is formed ; so that the reaction is really a cyclic process involving the alternate formation and decomposition of the intermediate compound. Starting with nitric acid, E. M. Péligot supposed that this compound is reduced to nitrogen peroxide : $2HNO_3+SO_2=H_2SO_4+2NO_2$; and that the nitrogen peroxide is reoxidized to nitric acid and nitric oxide : $3NO_2+H_2O=2HNO_3+NO$. The nitric oxide is then oxidized to nitrogen peroxide : $2NO+O_2=2NO_2$, which is then reduced to nitric oxide : $NO_2+SO_2+H_2O=H_2SO_4+NO$, and so on *ad infinitum*, or until the nitrogen oxide is dissolved and carried away by the sulphuric acid, or by the outgoing chamber gases. This theory was adopted by J. Kolb ; and J. Pelouze and E. Frémy, G. Lunge, G. E. Davis, E. Jackson, J. Mactear, J. Hurter, E. K. Muspratt, E. Sorel, and J. K. H. Inglis believed that the mechanical losses constitute the greater proportion of the total loss ; while G. Eschellman believed that 78 per cent. of the total loss is due to secondary chemical changes in the chambers. E. M. Péligot suggested that some nitrogen oxide is lost by a side reaction—reduction to nitrous oxide or nitrogen which can no longer take part in the cycle. F. Kuhlmann, however, said that under ordinary conditions the supposed side reaction : $2SO_2+2NO+2H_2O=2H_2SO_4+N_2$, does not occur ; and R. Weber, and E. Frémy said the same thing about the supposed side reaction : $3SO_2+2NO_2+3H_2O=3H_2SO_4+N_2O$. J. Pelouze, C. Irwin, R. Weber, and

G. Lunge showed that when in contact with water or dil. sulphuric acid, the higher nitrogen oxides are slowly reduced to inactive nitrous oxide by sulphur dioxide: $N_2O_4+3SO_2+3H_2O=3H_2SO_4+N_2O$; $N_2O_3+2SO_2+2H_2O=2H_2SO_4+N_2O$; and $2NO+SO_2+H_2O=N_2O+H_2SO_4$, in contact with a more conc. acid, these reactions take place very slowly or not at all. Consequently, these losses occur only when water or steam is in excess, or in the vicinity of the entering steam. C. Irwin said that the reactions: $2(NO_2)HSO_3+SO_2+2H_2O=3H_2SO_4+2NO$; and $2(NO_2)HSO_3+2SO_2+3H_2O=4H_2SO_4+N_2O$ may occur; and W. Hempel showed that in the presence of a large excess of sulphur dioxide and water, nitric oxide is almost completely reduced to nitrous oxide, only very small quantities of nitrogen are formed, and T. L. Bailey observed that in the presence of sulphuric acid the reduction of nitrous acid to nitrous oxide occurs provided the acid has a sp. gr. less than 1·225. Some reduction does occur; J. K. H. Inglis could account for only a 10 per cent. loss by reduction to nitrous oxide; W. Hempel and O. Heymann observed greater losses. It is, therefore, admitted that some of the active nitrogen oxide is reduced to a passive oxide; F. Raschig even went so far as to say that some reduced to ammonia, for he detected ammonia in the chamber acid when an excess of sulphur dioxide is present. In general, however, any ammonia present would react with nitrous acid to form nitrogen and water.

Returning to E. M. Péligot's hypothesis, J. J. Berzelius, and R. Weber raised the objection that sulphur dioxide is oxidized by nitric acid only at a high temp.—say 80°—and conc., and only a trifling oxidation occurs under the conditions which obtain in the lead chambers. J. J. Berzelius represented the cyclic reactions: $2SO_2+N_2O_4+2H_2O=2H_2SO_4+2NO$; and $2NO+O_2=N_2O_4$; while R. Weber gave $SO_2+N_2O_3+H_2O=H_2SO_4+NO$, and $4NO+O_2=2N_2O_3$; and W. C. Reynolds and W. H. Taylor, $SO_2+H_2O=H_2SO_3$; $H_2SO_3+NO_2=NO+H_2SO_4$; and $2NO+O_2=2NO_2$. These suggestions explain the facts as well as any other hypothesis which has been made. The early workers did not distinguish clearly between nitrogen trioxide and tetroxide; in what follows nitrogen tetroxide and nitrogen peroxide, as well as the formulæ NO_2 and N_2O_4, are used indiscriminately for the same compound. Nitrogen trioxide is the anhydride of nitrous acid, and R. Weber said that nitrous acid is the intermediate compound which oxidizes sulphur dioxide to sulphuric acid, forming nitric oxide. This occurs only when the nitrous acid is dissolved in water or in dil. sulphuric acid soln. which can be obtained by the dissolution of nitrogen trioxide or tetroxide. In the latter case nitric acid is formed at the same time; while dil. nitric acid has very little effect on sulphur dioxide at ordinary temp., but the acid with nitrogen tetroxide dissolved in it oxidizes vigorously. Nitric acid is not formed in the normal working of the chambers, nor in the acid from Gay Lussac's tower, hence the theory that the nitrous vapours are reduced down to nitric oxide is not in favour because the reoxidation of nitric oxide involves the formation of free nitrogen tetroxide and of nitric acid. There is another group of hypotheses in which imaginary intermediate compounds have been invented. The elusive and transient intermediate compound has not been isolated. F. Clément and J. B. Désormes surmised that water is necessary for the reaction, and they observed the formation of white crystals which gave out nitrogen oxide gas when treated with water, and they suspected that this compound plays a prominent part in the formation of sulphuric acid. H. Davy showed that the reaction proceeds only in the presence of water, and if insufficient water is present, crystals of nitrosylsulphuric acid, $(NO_2)HSO_3$, the so-called *chamber acid*—are formed. Consequently, H. Davy, F. H. de la Provostaye, L. Gmelin, C. Winkler, R. W. Hasenclever, and G. Lunge suggested that this is the intermediate compound. G. Lunge and co-workers showed that (1) dry nitric oxide, out of contact with sulphuric acid, unites with an excess of free oxygen to form nitrogen tetroxide, and if the nitric oxide be in excess, some nitrogen trioxide is also formed; (2) in the presence of moisture, nitric oxide and an excess of oxygen form nitric acid; (3) dil. sulphuric acid of sp. gr. 1·405 acts like water, but a small quantity of nitrous acid is formed—nitroxylsulphonic acid cannot exist in an acid of this conc. (4) If nitric oxide be slowly passed into sulphuric acid in the presence of oxygen, only that portion of the nitric oxide in immediate contact with the sulphuric acid is not oxidized beyond the nitrogen trioxide stage, but all the nitric oxide not in contact with the acid behaves like the dry gas in the presence of an excess of oxygen, and forms nitrogen tetroxide. Hence, in 1888, G. Lunge summarized his theory: sulphur dioxide combines directly with nitrogen trioxide, oxygen, and a little water to form nitroxylsulphonic acid which floats in the chamber as a mist; on meeting an excess of water, or dil. sulphuric acid, also floating about as a mist, the nitroxylsulphonic acid is split up into sulphuric acid, which settles to the bottom of the chamber, and nitrogen trioxide which begins to act again. Nitrogen trioxide, and not nitric oxide, is thus the carrier of oxygen. The formation of sulphuric acid is not brought about by the alternate oxidation of nitric oxide to nitrogen trioxide or tetroxide, which is subsequently reduced to nitric oxide, but rather by a cycle of reactions involving the condensation of nitrous acid with sulphur dioxide and oxygen to form nitroxylsulphonic acid: $2SO_2+N_2O_3+O_2+H_2O=2(NO_2)HSO_3$, followed by the splitting up of the nitroxylsulphonic acid by the excess of water, $2(NO_2)HSO_3+H_2O=2H_2SO_4+N_2O_3$, or $(NO_2)HSO_3+H_2O=H_2SO_4+HNO_3$; or $(SO_2+HNO_2+O)_{gas}=(NO_2.HSO_3)_{mist}$; and $(NO_2.HSO_3)_{mist}+H_2O=H_2SO_4+HNO_2$. If an excess of sulphur dioxide be present: $NO_2.HSO_3+SO_2+2H_2O=3H_2SO_4+2NO$, and the nitric oxide is oxidized by air to the trioxide. In favour of this hypothesis it is urged that the acid found in the chambers, the drips, and the bottom acid of the back chambers all contain nitroxylsulphuric acid. J. Hurter said that the relative amounts of acid formed in a series of chambers decrease approximately in geometrical progression from the first to the last chamber. The subject was studied by H. S. Smith, J. Mactear, N. Naef, G. Lunge and N. Naef, W. Crowder, and W. H. Maudsley. G. Lunge and N. Naef, A. Schertel, and S. Retter showed that the oxidation of the sulphur dioxide is rapid as far as the middle of the first chamber, after which it rapidly decreases; and there is an abrupt revival when the gases enter the second chamber. A. Schertel interprets this to mean that the mist of nitroxylsulphonic acid formed in the second half of the first chamber remains undecomposed owing to the scarcity of steam, and that there is consequently a deficiency of the catalytic agent. As the gases enter the second chamber, fresh steam decomposes the nitroxylsulphonic acid, nitrogen oxide is liberated, and there is a renewed activity; the mist of nitroxylsulphonic acid is again formed, and the reaction is suspended in the second chamber as in the analogous case in the first chamber. He said that nitroxylsulphonic acid is fairly stable, and requires a large proportion of steam for its decomposition. E. Sorel assumed that in addition to the main reaction: $2SO_2+2NO+3O+H_2O=2(NO_2)HSO_3$, a number of secondary reactions occur: $2NO+O=N_2O_3$; $NO+O=NO_2$; $2SO_2+N_2O_3+O_2+H_2O=2(NO_2)HSO_3$; $2SO_2+3N_2O_3+H_2O=2(NO_2)HSO_3+4NO$; and $2SO_2+4NO_2+H_2O=2NO+O+2(NO_2)HSO_3$. There are also the reactions $2(NO_2)HSO_3+H_2O=N_2O_3+2H_2SO_4$; $SO_2+N_2O_3+H_2O=H_2SO_4+2NO$. The objection has been raised by J. J. Berzelius, and R. Weber that all this does not prove that nitroxylsulphonic acid is the real intermediate compound when the chambers are working under normal conditions. W. C. Reynolds and W. H. Taylor say that it may be regarded as doubtful if nitroxylsulphonic acid—chamber crystals—plays an important part in the exchanges in the chambers themselves. E. Divers, indeed, expressed a doubt whether it is ever formed except by the action of sulphuric acid on one of the oxides of nitrogen, but as sulphurous acid reacts with soln. of chamber crystals, some sulphuric acid is possibly formed in this manner. Nitroxylsulphonic acid appears when there is a drought, *i.e.* a dearth of water. The nature of the intermediate compound may vary with the conditions of temp., and with the relative proportions of the reacting gases. Indeed, the cyclic of reactions may differ in different parts of the same chamber.

According to M. Neumann, the reactions in the Glover's tower and in the chamber furnish nitroxylsulphonic acid: $2SO_2+2NO+3O+H_2O=2(NO_2)HSO_3+(2x+20{\cdot}1)$ Cals., which occurs in two stages: $2NO+O=N_2O_3+20{\cdot}1$ Cals., and $2SO_2+N_2O_3+O_2+H_2O=2(NO_2)HSO_3+2x$ Cals. On the other hand, whereas in the chambers nitroxylsulphonic acid reacts: $2(NO_2)HSO_3+H_2O=2H_2SO_4+N_2O_3$, in the Glover's tower it reacts with water and sulphur dioxide: $2(NO_2)HSO_3+SO_2+2H_2O=3H_2SO_4+2NO+(x+3y-20{\cdot}1)$ Cals. This reaction occurs in two stages: $2(NO_2)HSO_3+H_2O=2H_2SO_4+N_2O_3+2y$ Cals., and $N_2O_3+SO_2+H_2O=H_2SO_4+2NO+(x+y-20{\cdot}1)$ Cals., where $x+y=54$ Cals. Since the denitration in the lower part of Glover's tower implies the endothermic reduction of a mol of nitrogen trioxide to 2 mols of nitric oxide with the absorption of 20·1 Cals., which are evolved again in the upper part of the tower, it is suggested that the operation be conducted in a series of towers, the upper parts of which are cooled and the lower parts are heated, while the apparatus is so arranged that as the ratio $O_2 : SO_2$ increases and consequently the tendency against the reduction of nitrogen trioxide to nitric oxide, the gases be heated to a correspondingly higher temp., to favour the endothermic reaction. G. Hering said that nitrogen trioxide reacts more quickly than nitrogen peroxide—if the former gas be really nitrogen trioxide (*q.v.*); this is taken to support G. Lunge's hypothesis.

F. Raschig elaborated a counter-hypothesis. He stated that in the presence of a large excess of oxygen, nitric oxide is converted to the trioxide, not the tetroxide, but this is not in agreement with the known instability of the trioxide (*q.v.*). However, G. Lunge showed that a mixture of nitric oxide and nitrogen tetroxide behaves towards sulphur dioxide the same as if it were nitrogen trioxide. F. Raschig assumed that dihydroxylamidosulphonic acid, $N(OH)_2.HSO_3$, or nitrosylsulphonic acid, $NO.HSO_3.H_2O$, is the intermediate compound formed by the union of nitrous and sulphurous acids: $HNO_2+SO_2=NO.HSO_3$; and this is decomposed by more nitrous acid into nitric oxide, and sulphuric acid: $NO.HSO_3+HNO_2=2NO+H_2SO_4$; and the nitric oxide is then oxidized to nitrous acid: $2NO+O+H_2O=2HNO_2$, and the cycle begins anew. If the sulphur dioxide is in excess hydroxyimidodisulphonic acid, $(HO)N(HSO_3)_2$, or nitrilotrisulphonic acid, $N(HSO_3)_3$, may be formed. G. Lunge objected that this hypothesis does not explain the presence of nitrogen tetroxide, and of nitroxylsulphonic acid in the lead chambers; and, further, that the reaction: $2NO+O+H_2O=2HNO_2$, does not occur since nitric acid is quantitatively formed. This is in agreement with the observations of M. Bodenstein, and of E. Briner and E. Fridöri. F. Raschig maintained that the constitution of nitroxylsulphonic acid is $O_2{\equiv}N-SO_2-OH$, and not $O=N-O-SO_2-OH$; and that reducing agents convert this into nitrosisulphonic acid, $O=N(OH)(HSO_3)$, with quadrivalent nitrogen: $NO.HSO_3+HNO_2=NO+NO(OH)(HSO_3)$, the hydroxynitrosylsulphonic acid easily breaks down into nitric oxide and sulphuric acid: $NO(OH)(HSO_3)=NO+H_2SO_4$. The hydroxynitrosylsulphonic acid (*q.v.*) was supposed by F. Raschig to be identical with the blue compound formed when an excess of sulphur dioxide is passed through a soln. of nitroxylsulphonic acid in conc. sulphuric acid, and the cause of the purple colour in the acid from Gay Lussac's tower when an excess of sulphur dioxide is present. A controversy between G. Lunge, and F. Raschig on the merits of their respective hypotheses was summarized by S. Hamburger, and W. Wyld, the general result of which is to show that F. Raschig's hypothesis is less probable because it is founded on too many questionable, auxiliary hypotheses, and that it does not explain the observed facts so well as G. Lunge's.

In 1904, E. Divers attempted a reconciliation. He said that sulphuric acid is produced in the lead chambers by a reaction between the liquid and gaseous parts of the mist, in which the two transient intermediaries, nitrosylsulphonic and nitroxylsulphonic acids, take part. The liquid particles of the mist consist of conc. sulphuric acid, holding nitroxysulphonic acid in soln., continually absorb sulphur dioxide and oxygen which, by the catalytic action of the nitroxylsulphonic acid, form sulphuric acid as fast as they are absorbed. Under normal conditions, sufficient water is absorbed partially to hydrolyze the nitroxylsulphonic acid, $ON.O.HSO_3$, into its constituent acids. Two mols of sulphur dioxide and one mol of oxygen are simultaneously absorbed because they find themselves between the NO-radicle of the catalyst—one moment as $NO.O.HSO_3$ and next moment as $NO.HSO_3$. Nitric oxide thus plays no direct part in the reactions, and the catalyst is alternately $NO.O.HSO_3$ and $NO.HSO_3$. In 1911, E. Divers favoured a modification of F. Raschig's hypothesis, and he believed that what F. Raschig called nitrosisulphonic acid has the composition $H_2N_2SO_6$, and that it is the only intermediate substance formed in the reaction: $2HNO_2+SO_2=H_2N_2SO_6$; and $H_2N_2SO_6=2NO+H_2SO_4$; and $2NO+O+H_2O=2HNO_2$—*vide supra.* C. W. Jurisch, W. Manchot, and W. C. Reynolds and W. H. Taylor have adversely criticized F. Raschig's hypothesis.

S. Littmann concluded that nitroxylsulphonic is not the main product of the intermediate reactions, but is rather an unavoidable evil. The intermediate compound is either hydroxyimidodisulphonic acid, or nitrosisulphonic acid. These are not formed, as F. Raschig assumed, by the oxidation of sulphur dioxide with nitrous acid, but by the action of nitric oxide: $2NO+2SO_2+O_2+2H_2O=2NO(OH).HSO_3$. This compound is resolved by water into nitric oxide and sulphuric acid. The oxidation of the nitric oxide, and the formation of the comparatively stable nitroxylsulphonic acid occur only when sulphur dioxide is in excess, or the supply of steam is impoverished.

W. Ostwald argued that the nitrous vapour acts as a catalyst in the lead chambers merely by increasing the speed of the otherwise slow and incomplete reaction: $SO_2+O+H_2O=H_2SO_4$. G. Lunge pointed out that in the case of sulphuric acid, this does not mean, as T. Meyer, and O. Wentzki assumed, that the intermediate reactions are mere by-reactions of minor importance. W. Ostwald probably meant that before accepting the assumption that the catalyst does its work through intermediary reactions, proof is required that the assumed intermediate reactions proceed faster than the direct reaction. J. Brode said that where a chemical reaction, as here, is dependent on two intermediate reactions of different velocities, the time occupied by the change is limited by the slower reaction. In the lead chamber, water is always present as a vapour, and as a liquid mist. The higher the temp., a larger proportion of the aqueous mist is converted into vapour. Nitroxylsulphonic acid requires liquid water for its decomposition, hence, as the proportion of liquid mist decreases, the velocity of one of the intermediate reactions must also decrease. The direct reaction is not reversible, nor is the reaction: $SO_2+HNO_2+O=NO_2.HSO_3$ reversible; but the reaction: $NO_2.HSO_3+H_2O\rightleftharpoons H_2SO_4+HNO_2$ is reversible. This means (i) that after the sulphur dioxide has all disappeared, some nitroxylsulphonic acid will remain undecomposed, particularly in the last chamber, where it is not practicable to employ sufficient water to decompose all the nitroxylsulphonic acid; and (ii) an excess of nitrogen oxides is needed in the last chamber if the oxidation of the sulphur trioxide is to be complete. The undecomposed nitroxylsulphonic acid is removed in Gay Lussac's tower.

E. Loew found that the chemical reactions in the chamber follow the mass law in that, with a constant temp., the speed of the reaction is proportional to the product of the active masses of the substances taking part in the change. The gases in each chamber reach in accord with the concentrations of the reacting molecules. T. Meyer attempted to apply the mass law, but, as emphasized by G. Lunge, and S. Haagn, not very successfully. F. Riedel attributed this to the fact that the temp. and concentrations are different in different parts of the chamber. O. F. Heymann found that the catalyst reacts from the first moment of its coming in contact with the mixture of sulphur dioxide, oxygen, and water-vapour; and he examined conditions for the efficient working of the chambers. A. Graire also studied the reversibility of the reactions in the chamber. Thus, sulphuric acid is reduced by nitric oxide. E. Briner and M. Rossignol found that with mixtures of sulphur dioxide, nitrogen peroxide, steam, oxygen, and variable proportions of nitrogen, the rate of formation of sulphuric acid increased with the conc. in such a way that the time needed to oxidize a given proportion of sulphur dioxide varied inversely as the square of the initial conc. From this, it follows that the reaction is of the third order. M. Forrer found that the order varied from 1·26 to 3·67; but if the conc. of the liquid phase did not vary the order was about 2. E. Briner and M. Rossignol showed that increasing the press. has the same effect on the speed of the reaction as increasing the conc.; and increasing the conc. of the nitrogen peroxide has an enormous effect in accelerating the reaction. Thus increasing the proportion of the peroxide from 0·5 to 2·43 per cent. increased the velocity about twelve-fold with mixtures containing 7·94–8·32 per cent. SO_2; 45·03–47·41 per cent. H_2O; 15·99–16·75 per cent. O_2; 26·12–27·02 per cent. N_2; along with 4·92, 4·27, 3·69, 2·46, 1·43, and 0·5 per cent. of NO_2, at 85°–86·5°, gave the results indicated in Fig. 79. E. Bitterli, and M. Forrer made some analogous measurements and found that the formation of sulphuric acid occurs only in the presence of a liquid phase, so that the system must be heterogeneous; the formation of the acid takes place in a shorter time and the yield is increased if a liquid, either sulphuric acid or water, is present at the outset. Further, the rate at which water is supplied during the course of the reaction exerts a considerable effect both on the velocity of reaction and on the conc. of the product. Under certain conditions, the acid formed may disappear, which is taken to indicate that the reactions assumed to take place in the chambers are at least partly reversible. For a low conc. of the gases, there is an optimum rate of intake for water vapour: this gives the best yield and, at the same time, the most conc. acid. As the gas conc. increases, the optimum point shifts in the direction of diminution of water supply. The relation between the speed of the reaction (grams H_2SO_4 per hour) and the conc. of the gases (per cent. SO_2 by vol.) is illustrated by Fig. 80. This relation is much less complex when the composition of the liquid phase is constant. It is inferred that an intermediate compound is formed in which water is a constituent, but it is decomposed by water. The rate of the reaction is almost unaffected by the supply of sulphur dioxide. W. Hempel also made some measurements on the speed of the reaction with sulphur dioxide, oxygen, water vapour, and nitrogen oxides. The reaction with nitrogen trioxide is faster than with the peroxides. O. Wentzki questioned the validity of this observation in establishing the existence of any particular theory of intermediate reaction. W. Hempel found that with a high concentration of nitrogen oxides, the optimum temp. is 70°. The subject has been discussed by B. Waeser.

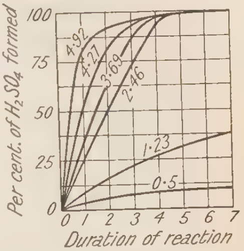

Fig. 79.—The Effect of Nitrogen Peroxide on the Rate of Oxidation of Sulphur Dioxide.

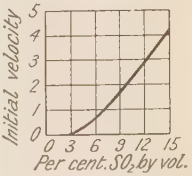

Fig. 80.—The Relation between the Rate of Formation of Sulphuric Acid and the Concentration of the Reacting Gases.

The contact process of manufacture.—In this process—indicated in connection with sulphur trioxide—a mixture of sulphur dioxide and air from the *burners* must be very carefully cleaned from dust, finely-divided sulphur, sulphuric acid, arsenic, etc., otherwise the platinized asbestos soon becomes inactive. Arsenic is particularly injurious. The gases are accordingly cleaned by passage through a chamber—the *dust chamber*—in which steam is injected; through a series of lead pipes to reduce the temperature down to about 100°; through a series of towers in each of which the gases meet a descending spray of water. This washes the sulphuric acid, etc., from the gas. Finally, the gases are dried by passing them up to a tower where they meet a descending stream of conc. sulphuric acid. The gases are periodically tested for dust, arsenic, etc., to make sure the scrubbers, etc., are working efficiently. The dried gases then pass into the *contact chamber*. In outline, this chamber consists of a cylinder which contains a number of tubes each packed with platinized asbestos placed between perforated shelves. The dry mixture of sulphur dioxide and air enters the contact chamber through a series of perforations near the base; and, after passing up to the top of the cylinder around the outside of the tubes containing the platinized asbestos, the gases descend through the platinized asbestos (where oxidation takes place), and leave the apparatus. The platinized asbestos is arranged in this particular manner to avoid local rise of temp. by the heat evolved during the reaction: $2SO_2+O_2=2SO_3+45{\cdot}2$ Cals. Hence, the system has a tendency to become hotter during the oxidation. Since the best results are obtained when the temp. of the asbestos is in the vicinity of 400°, everything is arranged so that the asbestos tubes are at first heated to the necessary temp. by externally applied heat, and afterwards maintained at this temp. by the cold gases ascending in the interior of the cylinder. Experience shows that 96–98 per cent. of the sulphur dioxide can be oxidized in the contact chamber. The white mist—*vide infra*—of sulphur trioxide is absorbed with great difficulty by water or dil. sulphuric acid; but it is rapidly and completely absorbed by 97–98 per cent. sulphuric acid. Hence, the gases which leave the contact chamber pass into the *condensing tanks* which are made of cast-iron, and contain 97–98 per cent. sulphuric acid. A stream of water or dil. acid is run into the condensing tanks at such a rate that the concentration of the acid is maintained at 97–98 per cent. If fuming acid be required, one or more wrought-iron absorbing vessels are placed between the condensing tanks and the contact chamber. Manufacturing details are indicated in monographs by F. D. Miles,[43] etc.

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§ 30. The Physical Properties of Sulphuric Acid

Conc. sulphuric acid with about 35 per cent. of free sulphur trioxide is solid at ordinary temp. ; with 60 per cent., it is liquid ; and with 80 per cent., solid—*vide supra*, Fig. 78. The most conc. acid obtained by boiling the ordinary purified acid was stated by A. Bineau [1] to contain 99 per cent. H_2SO_4 ; J. C. G. de Marignac gave 98·86 to 98·54 per cent. ; L. Pfaundler and A. Pölt, 98·45 ; A. Schertel, 98·66 ; H. E. Roscoe, 98·4–98·8 ; W. Dittmar, 98·20–98·99 ; and R. Knietsch, about 98·3. G. Lunge and P. Naef could not obtain a concentration higher than 98·6 per cent. H_2SO_4 by evaporation in vacuo. G. Lunge's 98·3 per cent. is usually accepted as the best representative value. It solidifies just below 0°. The commercial conc. acid contains 94–97 per cent. H_2SO_4. The so-called *brown oil of vitriol—B.O.V.*—has about 79 per cent. H_2SO_4 ; *rectified oil of vitriol—R.O.V.*—or *double oil of vitriol—D.O.V.*—has 93·0–95·0 per cent. H_2SO_4, and, if the arsenic has been previously removed, it is called *distilled oil of vitriol*, although this is not what is commonly understood by a distilled liquid. With fuming sulphuric acid the total sulphuric trioxide is distributed as follows :

Total SO_3 .	81·6326	81·8163	83·4693	85·3061	87·1428	88·9795 per cent.
H_2SO_4 .	100	99	90	80	70	60 per cent.
SO_3 free	0	1	10	20	30	40 per cent.
Total SO_3 .	90·8163	92·6530	94·4897	96·3265	98·1632	99·8163 per cent.
H_2SO_4 .	50	40	30	20	10	1 per cent.
SO_3 free	50	60	70	80	90	99 per cent.

In order to obtain an acid with a smaller proportion of sulphur trioxide by diluting it with ordinary sulphuric acid, let x denote the amount of H_2SO_4 to be added to make 100 parts of the fuming acid ; a, the total SO_3 per 100 parts of the desired acid ; b, the total SO_3 in 100 parts of the fuming acid to be diluted ; and c, the SO_3 in 100 parts of the sulphuric acid to be added as diluent, then M. Gerstner gave $x(a-c)=100(b-a)$. E. F. Anthon also discussed the preparation of soln. of a given sp. gr. by mixing the conc. acid with water. According to A. Marshall, if S denotes the sp. gr. of sulphuric acid at 15°, the percentage amount of H_2SO_4 is $86S-69{\cdot}00$. E. Biron found that 1 c.c. of a soln. of sulphuric acid at 20° contains pD 4903·8 gram-equivalents H_2SO_4, where D denotes the sp. gr. at 20°/4°, and p, the percentage amount of H_2SO_4. A. H. W. Aten discussed the preparation of sulphuric acid of known strengths from sp. gr. determinations.

The tendency of sulphuric acid to **undercooling** was indicated in connection with the study of the different hydrates. J. G. Grenfell [2] studied the **supersaturation** of soln. of the sulphates ; and J. M. Thomson, the isomorphous **crystallization** of the sulphates. S. Pagliani found that during the electrolysis of soln. of some of the sulphates, the salt crystallizes on the anode, when this is made from the corresponding metal and does not exceed 40 sq. cm. per ampère. When conc. soln. are used, the strength of the current at the anode is not the same for the different salts. The maximum value of the strength of current, with which this phenomenon occurs, is, for differently conc. soln. of one and the same salt, the greater the more dil. the soln. This value depends also very much on the temp. as it increases as the latter rises. The strength of the current at the cathode is of no influence. H. M. Vernon discussed the **colour** of soln. of the sulphates ; and J. Moir, of soln. of various substances in sulphuric acid soln.

C. A. Cameron and J. Macallan, and J. A. C. Chaptal described the crystals as six-sided prisms terminating in pyramids with six faces, and T. Graham described the habit as six-sided prisms of a tabular form ; both agree that the crystals belong to the hexagonal system. C. A. Cameron and J. Macallan found that the monohydrate, $H_2SO_4.H_2O$, at ordinary temp., is a colourless, transparent, oily liquid, which, when cooled, furnishes hexagonal crystals; J. C. G. de Marignac, and T. Graham said that the dihydrate, $H_2SO_4.2H_2O$, yields colourless, transparent six-sided prisms which J. I. Pierre and E. Puchot called monoclinic. The crystals of sulphuric acid were also studied by J. Levallois.

A large number of determinations of the **specific gravity** of sulphuric acid have been made. Among the early observations are those by J. Dalton,[2] D. G. Fahrenheit, R. Kirwan, S. Parkes, A. Ure, L. N. Vauquelin, J. P. J. d'Arcet, P. T. Meissner, H. Hager, T. Graham, M. Debezenne, A. Bussy and H. Buignet, T. Thomson, J. A. Wanklyn and J. Robinson, J. B. Richter, M. J. J. Dize, A. Bineau, V. A. Jacquelain, C. Langberg, V. S. M. van der Willigen, etc. Other determinations have been made of sp. gr. as one of the factors involved in the determination of other physical constants by M. le Blanc and P. Rohland, E. Ruppin, J. Wagner, A. E. Dunstan and R. W. Wilson, J. Forchheimer, D. Sidersky, H. T. Barnes and A. P. Scott, G. Forch, E. H. Loomis, O. Grotrian, W. Ostwald, A. Schulze, P. Kremers, B. C. Felipe, V. F. Hess, G. W. Muncke, W. C. Röntgen and F. Schneider, W. H. Perkin, J. Thomsen, F. Kohlrausch, W. Kohlrausch, G. A. Hagemann, H. D. Holler and E. L. Peffer, R. Schenck, H. C. Jones and co-workers, V. F. Hess, C. Chéneveau, F. Schöttner, F. Schwers, M. Berthelot, F. Zecchini, etc. Observations on the fuming acid were made by A. Chapman and R. Messel, R. Knietsch, etc. C. Winkler's results for the sp. gr. and total content of SO_3, from 15° to 35°, for fuming sulphuric acid, made by the old dry distillation process, are indicated in Table VII. R. Knietsch gave the results in Table VIII for fuming acid, from 15° to 45°, made by the contact process.

TABLE VII.—THE SPECIFIC GRAVITY OF FUMING SULPHURIC ACID FROM 15° TO 35° (NORDHAUSEN PROCESS).

Total SO_3 per cent.	Sp. gr. at				
	15°	20°	25°	30°	35°
76·67	1·8417	1·8371	1·8323	1·8387	1·8240
77·49	1·8427	1·8378	1·8333	1·8295	1·8249
78·34	1·8428	1·8388	1·8351	1·8302	1·8255
79·04	1·8437	1·8390	1·8346	1·8300	1·8257
79·99	1·8427	1·8386	1·8351	1·8297	1·8250
80·46	1·8420	1·8372	1·8326	1·8281	1·8234
80·94	1·8398	1·8350	1·8305	1·8263	1·8218
81·37	1·8446	1·8400	1·8353	1·8307	1·8262
81·91	1·8509	1·8466	1·8418	1·8371	1·8324
82·17	1·8571	1·8522	1·8476	1·8432	1·8385
92·94	1·8697	1·8647	1·8595	1·8545	1·8498
83·25	1·8790	1·8742	1·8687	1·8640	1·8592
83·84	1·8875	1·8823	1·8767	1·8713	1·8661
84·12	1·8942	1·8888	1·8833	1·8775	1·8722
84·33	1·8990	1·8940	1·8890	1·8830	1·8772
84·67	1·9034	1·8984	1·8930	1·8874	1·8820
84·82	1·9072	1·9021	1·8950	1·8900	1·8845
84·99	1·9095	1·9042	1·8986	1·8932	1·8866
85·14	1·9121	1·9053	1·8993	1·8948	1·8892
85·54	1·9250	1·9193	1·9135	1·9082	1·9023
85·68	1·9290	1·9236	1·9183	1·9129	1·9073
85·88	1·9368	1·9310	1·9250	1·9187	1·9122
86·51	1·9447	1·9392	1·9334	1·9279	1·9222
86·72	1·9520	1·9465	1·9402	1·9338	1·9278
87·03	1·9584	1·9528	1·9466	1·9406	1·9340
87·46	1·9632	1·9573	1·9518	1·9457	1·9398
88·82	Cryst	Cryst	1·9740	1·9666	1·9600

Table VIII.—The Specific Gravity of Fuming Sulphuric Acid from 15° to 45° (Contact Process).

SO_3		Sp. gr.		
Total.	Free.	15°	35°	45.°
81·63	0·0	1·8500	1·8186	1·822
83·46	10·0	1·888	1·8565	1·858
85·30	20·0	1·920	1·8919	1·887
87·14	30·0	1·957	1·9280	1·920
88·97	40·0	1·979	1·9584	1·945
90·81	50·0	2·009	1·9733	1·964
92·65	60·0	2·020	1·9738	1·959
94·48	70·0	2·018	1·9564	1·942
96·32	80·0	2·008	1·9251	1·890
98·16	90·0	1·990	1·8888	1·864
100·00	100·0	1·984	1·8370	1·814

For 100 per cent. H_2SO_4, R. Knietsch gave 1·8500 at 15°; 1·8186 at 35 °; and 1·822 at 45°. J. C. G. de Marignac said that the acid with about 98 per cent. H_2SO_4 corresponds with a maximum on the sp. gr. curve, and D. P. Konowaloff, with a minimum on the vap. press. curve. For the crystals of monohydrate, $H_2SO_4.H_2O$, at 0°/4°, A. Bineau gave 1·951, and 1·792 for the liquid. J. A. C. Chaptal gave 1·780 for the liquid; H. W. F. Wackenroder, 1·784; V. A. Jacquelain, 1·7858 D. I. Mendeléeff, 1·7943; R. S. Tjaden-Moddermann, 1·783 at 10°; and R. Pictet, 1·777. For the dihydrate, $H_2SO_4.2H_2O$, T. Graham gave 1·6321; V. A. Jacquelain, 1·6746; A. Bineau, 1·665 at 0°; D. I. Mendeléeff, 1·6655 at 0°/4°; and R. Pictet, 1·650. Observations for the sp. gr. of soln. of sulphuric acid and water were given by R. Kirwan, A. Ure, L. N. Vauquelin, J. P. J. d'Arcet, A. Bineau, J. Kolb, G. Lunge and P. Naef, G. Lunge and M. Isler, S. U. Pickering, A. Smits and co-workers, J. R. Katz, A. Marshall, J. R. Pound, H. D. Richmond, W. C. Ferguson, G. Tammann, etc. J. Domke and W. Bein gave the results indicated in Table IX, where *N* refers to the eq. normality of the soln. at 15° when 1 eq. has 49·04 grms. H_2SO_4 per litre. The results in Table IX are calculated from the

Table IX.—Specific Gravities of Solutions of Sulphuric Acid between 0° and 50°.

H_2SO per cent.	0°	5°	10°	15°	20°	25°	30°	40°	50°	*N*
0	0·9999	1·0000	0·9997	0·9991	0·9982	0·9971	0·9957	0·9922	0·9881	0·000
1	1·0075	1·0073	1·0069	1·0061	1·0051	1·0038	1·0022	0·9986	0·9944	0·205
2	1·0147	1·0144	1·0138	1·0129	1·0118	1·0104	1·0087	1·0050	1·0006	0·413
3	1·0219	1·0214	1·0206	1·0197	1·0184	1·0169	1·0152	1·0113	1·0067	0·624
4	1·0291	1·0284	1·0275	1·0264	1·0250	1·0234	1·0216	1·0176	1·0129	0·837
5	1·0364	1·0355	1·0344	1·0332	1·0317	1·0300	1·0281	1·0240	1·0192	1·053
6	1·0437	1·0426	1·0414	1·0400	1·0384	1·0367	1·0347	1·0305	1·0256	1·272
7	1·0511	1·0498	1·0485	1·0469	1·0453	1·0434	1·0414	1·0371	1·0321	1·494
8	1·0585	1·0571	1·0556	1·0539	1·0522	1·0502	1·0482	1·0437	1·0386	1·719
9	1·0660	1·0644	1·0628	1·0610	1·0591	1·0571	1·0549	1·0503	1·0451	1·947
10	1·0735	1·0718	1·0700	1·0681	1·0661	1·0640	1·0617	1·0570	1·0517	2·178
11	1·0810	1·0792	1·0773	1·0753	1·0731	1·0709	1·0686	1·0637	1·0584	2·412
12	1·0886	1·0866	1·0846	1·0825	1·0803	1·0780	1·0756	1·0705	1·0651	2·649
13	1·0962	1·0942	1·0920	1·0898	1·0874	1·0851	1·0826	1·0774	1·0719	2·889
14	1·1039	1·1017	1·0994	1·0971	1·0947	1·0922	1·0897	1·0844	1·0788	3·132
15	1·1116	1·1093	1·1069	1·1045	1·1020	1·0994	1·0968	1·0914	1·0857	3·378

H_2SO per cent.	0°	5°	10°	15°	20°	25°	30°	40°	50°	*N*
16	1·1194	1·1170	1·1145	1·1120	1·1094	1·1067	1·1040	1·0985	1·0927	3·628
17	1·1272	1·1247	1·1221	1·1195	1·1168	1·1141	1·1113	1·1057	1·0998	3·881
18	1·1351	1·1325	1·1298	1·1270	1·1243	1·1215	1·1187	1·1129	1·1070	4·137
19	1·1430	1·1403	1·1375	1·1347	1·1318	1·1290	1·1261	1·1202	1·1142	4·396
20	1·1510	1·1481	1·1453	1·1424	1·1394	1·1365	1·1335	1·1275	1·1215	4·659
21	1·1590	1·1560	1·1531	1·1501	1·1471	1·1441	1·1411	1·1350	1·1288	4·925
22	1·1670	1·1640	1·1609	1·1579	1·1548	1·1517	1·1486	1·1424	1·1362	5·194
23	1·1751	1·1720	1·1688	1·1657	1·1626	1·1594	1·1563	1·1500	1·1437	5·467
24	1·1832	1·1800	1·1768	1·1736	1·1704	1·1672	1·1640	1·1576	1·1512	5·744
25	1·1914	1·1881	1·1848	1·1816	1·1783	1·1751	1·1718	1·1653	1·1588	6·024
26	1·1996	1·1962	1·1929	1·1896	1·1863	1·1829	1·1796	1·1730	1·1665	6·307
27	1·2078	1·2044	1·2010	1·1976	1·1942	1·1909	1·1875	1·1808	1·1742	6·594
28	1·2161	1·2126	1·2091	1·2057	1·2023	1·1989	1·1955	1·1887	1·1820	6·884
29	1·2243	1·2208	1·2173	1·2138	1·2104	1·2069	1·2035	1·1966	1·1898	7·178
30	1·2326	1·2291	1·2255	1·2220	1·2185	1·2150	1·2115	1·2046	1·1978	7·476
31	1·2410	1·2374	1·2338	1·2302	1·2267	1·2232	1·2196	1·2127	1·2057	7·777
32	1·2493	1·2457	1·2421	1·2385	1·2349	1·2314	1·2278	1·2207	1·2137	8·082
33	1·2577	1·2541	1·2504	1·2468	1·2432	1·2396	1·2360	1·2289	1·2219	8·390
34	1·2661	1·2625	1·2588	1·2552	1·2515	1·2479	1·2443	1·2371	1·2300	8·702
35	1·2746	1·2709	1·2672	1·2636	1·2599	1·2563	1·2527	1·2454	1·2383	9·018
36	1·2831	1·2794	1·2757	1·2720	1·2684	1·2647	1·2610	1·2538	1·2466	9·338
37	1·2917	1·2880	1·2843	1·2806	1·2769	1·2732	1·2695	1·2622	1·2549	9·662
38	1·3004	1·2966	1·2929	1·2891	1·2854	1·2817	1·2780	1·2707	1·2634	9·989
39	1·3091	1·3053	1·3016	1·2978	1·2941	1·2904	1·2866	1·2793	1·2719	10·322
40	1·3179	1·3141	1·3103	1·3065	1·3028	1·2991	1·2953	1·2879	1·2806	10·657
41	1·3267	1·3229	1·3191	1·3153	1·3116	1·3078	1·3041	1·2967	1·2893	10·997
42	1·3357	1·3318	1·3280	1·3242	1·3204	1·3167	1·3129	1·3055	1·2981	11·341
43	1·3447	1·3408	1·3370	1·3332	1·3294	1·3250	1·3218	1·3144	1·3070	11·690
44	1·3538	1·3500	1·3461	1·3423	1·3384	1·3346	1·3309	1·3234	1·3160	12·043
45	1·3631	1·3592	1·3553	1·3514	1·3476	1·3438	1·3400	1·3325	1·3250	12·401
46	1·3724	1·3685	1·3646	1·3607	1·3569	1·3530	1·3942	1·3417	1·3342	12·764
47	1·3819	1·3779	1·3740	1·3701	1·3663	1·3624	1·3586	1·3510	1·3435	13·131
48	1·3915	1·3875	1·3836	1·3796	1·3757	1·3719	1·3680	1·3604	1·3528	13·504
49	1·4012	1·3972	1·3932	1·3893	1·3853	1·3814	1·3776	1·3699	1·3623	13·881
50	1·4110	1·4070	1·4030	1·3990	1·3951	1·3911	1·3872	1·3795	1·3719	14·264
51	1·4209	1·4169	1·4128	1·4088	1·4049	1·4009	1·3970	1·3893	1·3816	14·652
52	1·4310	1·4269	1·4228	1·4188	1·4148	1·4109	1·4069	1·3991	1·3914	15·045
53	1·4411	1·4370	1·4330	1·4289	1·4249	1·4209	1·4169	1·4091	1·4013	15·443
54	1·4514	1·4473	1·4432	1·4391	1·4350	1·4310	1·4270	1·4191	1·4113	15·846
55	1·4618	1·4577	1·4535	1·4494	1·4453	1·4412	1·4327	1·4203	1·4214	16·255
56	1·4724	1·4681	1·4640	1·4598	1·4557	1·4516	1·4475	1·4395	1·4317	16·670
57	1·4830	1·4787	1·4745	1·4703	1·4662	1·4620	1·4580	1·4499	1·4420	17·090
58	1·4937	1·4894	1·4851	1·4809	1·4767	1·4726	1·4685	1·4604	1·4524	17·515
59	1·5045	1·5002	1·4959	1·4916	1·4874	1·4832	1·4791	1·4709	1·4629	17·946
60	1·5154	1·5111	1·5067	1·5024	1·4982	1·4940	1·4898	1·4816	1·4735	18·382
61	1·5264	1·5220	1·5177	1·5133	1·5091	1·5048	1·5006	1·4923	1·4842	18·824
62	1·5376	1·5331	1·5287	1·5243	1·5200	1·5157	1·5115	1·5031	1·4949	19·272
63	1·5487	1·5442	1·5389	1·5354	1·5310	1·5267	1·5224	1·5140	1·5058	19·275
64	1·5600	1·5555	1·5510	1·5465	1·5421	1·5378	1·5335	1·5250	1·5167	20·183
65	1·5713	1·5668	1·5622	1·5578	1·5533	1·5490	1·5446	1·5361	1·5277	20·647
66	1·5828	1·5782	1·5736	1·5691	1·5464	1·5602	1·5558	1·5472	1·5388	21·117
67	1·5943	1·5896	1·5850	1·5805	1·5760	1·5715	1·5671	1·5584	1·5499	21·593
68	1·6058	1·6012	1·5965	1·5919	1·5874	1·5829	1·5784	1·5697	1·5611	22·075
69	1·6175	1·6128	1·6081	1·6035	1·5989	1·5944	1·5899	1·5811	1·5725	22·562
70	1·6293	1·6245	1·6198	1·6151	1·6015	1·6059	1·6014	1·5925	1·5838	23·054

H_2SO per cent	0°	5°	10°	15°	20°	25°	30°	40°	50°	*N*
71	1·6411	1·6363	1·6315	1·6268	1·6221	1·6175	1·6130	1·6040	1·5952	23·553
72	1·6529	1·6481	1·6433	1·6385	1·6339	1·6292	1·6246	1·6156	1·6067	24·057
73	1·6649	1·6600	1·6551	1·6503	1·6456	1·6409	1·6363	1·6271	1·6182	24·567
74	1·6768	1·6719	1·6670	1·6622	1·6574	1·6526	1·6480	1·6387	1·6297	25·082
75	1·6888	1·6838	1·6789	1·6740	1·6692	1·6644	1·6597	1·6503	1·6412	25·602
76	1·7008	1·6958	1·6908	1·6858	1·6810	1·6761	1·6713	1·6619	1·6526	26·126
77	1·7127	1·7077	1·7026	1·6976	1·6927	1·6878	1·6829	1·6734	1·6640	26·655
78	1·7247	1·7195	1·7144	1·7093	1·7043	1·6994	1·6944	1·6847	1·6751	27·188
79	1·7365	1·7313	1·7261	1·7209	1·7159	1·7108	1·7058	1·6959	1·6862	27·724
80	1·7482	1·7429	1·7376	1·7324	1·7272	1·7221	1·7170	1·7069	1·6971	28·621
81	1·7597	1·7542	1·7489	1·7435	1·7383	1·7331	1·7279	1·7177	1·7077	28·799
82	1·7709	1·7654	1·7599	1·7544	1·7491	1·7437	1·7385	1·7281	1·7180	29·336
83	1·7816	1·7759	1·7704	1·7549	1·7594	1·7540	1·7487	1·7382	1·7279	29·871
84	1·7916	1·7860	1·7804	1·7748	1·7693	1·7639	1·7585	1·7479	1·7375	30·401
85	1·8009	1·7953	1·7897	1·7841	1·7786	1·7732	1·7678	1·7571	1·7466	30·924
86	1·8095	1·8039	1·7983	1·7927	1·7872	1·7818	1·7763	1·7657	1·7552	31·438
87	1·8173	1·8117	1·8061	1·8006	1·7951	1·7897	1·7843	1·7736	1·7632	31·943
88	1·8243	1·8187	1·8132	1·8077	1·8022	1·7968	1·7915	1·7809	1·7705	32·438
89	1·8306	1·8250	1·8195	1·8141	1·8087	1·8033	1·7979	1·7874	1·7770	32·922
90	1·8361	1·8306	1·8252	1·8198	1·8144	1·8091	1·8038	1·7933	1·7829	33·397
91	1·8410	1·8356	1·8302	1·8248	1·8195	1·8142	1·8090	1·7986	1·7883	33·862
92	1·8453	1·8399	1·8346	1·8293	1·8240	1·8188	1·8136	1·8033	1·7932	34·318
93	1·8490	1·8437	1·8384	1·8331	1·8279	1·8227	1·8176	1·8074	1·7974	34·764
94	1·8520	1·8467	1·8415	1·8363	1·8312	1·8260	1·8210	1·8110	1·8011	35·199
95	1·8544	1·8491	1·8439	1·8388	1·8337	1·8286	1·8236	1·8137	1·8040	35·622
96	1·8560	1·8508	1·8457	1·8406	1·8355	1·8305	1·8255	1·8157	1·8060	36·030
97	1·8569	1·8517	1·8466	1·8414	1·8364	1·8314	1·8264	1·8166	1·8071	36·421
98	1·8567	1·8515	1·8463	1·8411	1·8361	1·8310	1·8261	1·8163	1·8068	36·791
99	1·8551	1·8498	1·8445	1·8393	1·8342	1·8292	1·8242	1·8145	1·8050	37·132
100	(1·8517)	(1·8463)	(1·8409)	(1·8357)	(1·8305)	(1·8255)	(1·8205)	(1·8107)	(1·8013)	(37·433)

values at 15°, and the data at 15° were determined with reference to water at 4° when the sp. gr. of water at 15° is 1·000868. D. I. Mendeléeff observed that for $H_2SO_4+nH_2O$ the sp. gr. at 0°, referred to water at 4°, in vacuo, are :

n . .	400	200	100	50	25	12·5	10	5
Sp. gr. .	1·0099	1·0192	1·0372	1·0716	1·1336	1·12345	1·2760	1·4314
n . .	2·5	2	1	0·5	0	−0·2	−0·4	
Sp. gr. .	1·6102	1·6655	1·7943	1·8435	1·8528	1·9075	1·9793	

He represented the sp. gr., S, of the soln., water at 1000, ranging from water to $n=150$, $S=9998·7+76·51p-1·325p^2$, where p denotes the percentage amount of H_2SO_4 ; and for n between 150 and 6, $S=9998·7+71·16p+0·02035p^2$; for n between 6 and 2, $S=9998·7+61·908p+0·3980p^2$; for n between 2 and 1, $S=326·65p-1·3525p^2$; for n between 1 and 0, $S=18528+20·445(100-p)-3·746(100-p)^2$; and for the fuming acid, $S=18528+129(p-100)+3·9(p-100)^2$. J. L. R. Morgan and C. E. Davis found that when the sp. gr. and the deviations from the mixture rule are plotted, Fig. 81, the resulting curve shows breaks corresponding with the hydrates $H_2SO_4.H_2O$ and $H_2SO_4.12H_2O$. E. H. Loomis gave 1·0306 for the sp. gr. of N-H_2SO_4 at 15°. For soln. of a very low conc. F. Kohlrausch gave for the sp. gr. of soln. at 5·96° containing N-grm. eq. H_2SO_4 per litre :

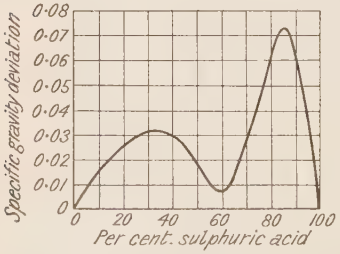

Fig. 81.—Specific Gravity Deviations of Sulphuric Acid from Mixture Rule.

N .	0·000203	0·000607	0·001011	0·002010	0·005037	0·010026	0·04994	0·09908
Sp. gr.	$1{\cdot}0_{5}88$	$1{\cdot}0_{4}266$	$1{\cdot}0_{4}442$	$1{\cdot}0_{4}870$	$1{\cdot}0_{3}2132$	$1{\cdot}0_{3}4158$	1·0019	0·003669

S. U. Pickering's differentiation of sp. gr. curve furnishes seventeen straight lines indicating that the sp. gr. is a complex of 17 parabolic components which were assumed to represent the sp. gr. curves of 17 hydrates in soln.—*vide supra.* J. R. Pound measured the sp. gr. of mixtures of sulphuric acid and ether. F. Kohlrausch found that the **maximum density** of mixtures of sulphuric acid and water occurs with 2 per cent. of water; H. D. Richmond said 2·5 per cent. of water; R. Knietsch, 2·34 per cent. of water; and J. Domke and W. Bein, 2·75 per cent. of water when the sp. gr. is 1·8415. C. M. Despretz said that with *p* per cent. of sulphuric acid the temp., $\theta°$, of maximum density is:

p . . .	0·62	1·23	2·45	3·57	6·81
θ . .	2·18°	0·60°	−1·92°	−5·0°	−13·7°

G. Tammann discussed the effect of *pressure* on the temp. of maximum density. According to A. Bineau, the effect of *temperature* is such that if the sp. gr., *S*, be determined at $\theta°$, the sp. gr., S_0, at 0° is $S_0=144{\cdot}38S/(144{\cdot}38-\theta)$. C. E. Linebarger gave the following data:

Per cent. H_2SO_4	0°	10°	20°	30°	40°	50°	60°	70°
2·65	1·021	1·019	1·017	1·015	1·013	1·011	—	—
11·87	1·081	1·078	1·075	1·072	1·069	1·066	—	—
18·33	1·138	1·133	1·128	1·125	1·123	1·118	1·113	1·108
35·13	1·275	1·268	1·262	1·255	1·248	1·242	1·235	1·228
58·05	1·494	1·486	1·478	1·470	1·462	1·454	1·446	1·438
65·27	1·575	1·567	1·559	1·531	1·543	1·535	1·527	1·519
80·45	1·752	1·743	1·734	1·725	1·716	1·707	1·698	1·689
83·23	1·783	1·774	1·764	1·755	1·746	1·737	1·728	1·718
95·02	1·843	1·833	1·824	1·814	1·805	1·796	1·786	1·775

D. I. Mendeléeff said that the variation of the sp. gr. with temp. follows the rule $S=S_0(1-\alpha\theta)$, where α is the coeff. of expansion. For 99·5 per cent. H_2SO_4, J. Domke and W. Bein gave for the sp. gr. *S* at $\theta°$, $S=S_{15}-0{\cdot}001035(\theta-15)+0{\cdot}0000015(\theta-15)^2$. For an acid of sp. gr. *S* at 0°, the decrease, δ, in the sp. gr. for a rise of 10° is:

S .	1·04	1·07	1·10	1·15	1·20	1·30	1·45	1·70	1·85
δ .	0·002	0·003	0·004	0·005	0·006	0·007	0·008	0·009	0·0096

or, in an analogous way, for an acid of sp. gr. *S*, at 15°, a correction δ per degree must be made:

S .	1·000–1·170	1·170–1·450	1·450–1·580	1·580–1·750	1·750–1·820	1·820–1·840
δ .	0·0006	0·0007	0·0008	0·0009	0·0010	0·0008

The sp. gr. in the tables refer to purified sulphuric acid, the ordinary commercial acids always contain *impurities* which usually raise the sp. gr. Thus, R. Kissling found that sulphuric acid containing arsenic trioxide had the following sp. gr. at 15° and the indicated percentages of H_2SO_4, and As_2O_3:

Sp. gr. .	1·8367	1·8373	1·8393	1·8412	1·8413	1·8414	1·8415
H_2SO_4 .	93·83	93·12	92·87	94·25	93·60	93·93	93·77
As_2O_3 .	0·024	0·028	0·192	0·219	0·254	0·231	0·231

when G. Lunge and P. Naef's values for the purified acid were:

Sp. gr. .	1·833	1·834	1·835	1·837	1·838	1·839	1·840
H_2SO_4 .	92·75	93·05	93·43	94·20	94·60	95·00	95·60

J. T. Dunn measured the effect of sulphur dioxide on sulphuric acid of sp. gr. 1·841 and found that with 33·73 vols. of SO_2 at n.p. θ, the sp. gr. was 1·823; with 19·27 vols., 1·822; and with 4·54 vols., 1·809. A. Marshall found that with mixtures of nitric acid the sp. gr. increases up to 1·862 and 7·5 per cent. of HNO_3, and thereafter the sp. gr. decreases, 0·1 per cent. of lead sulphate raised the sp. gr. 0·0015; of arsenic trioxide, 0·0013; of nitrosulphuric acid, 0·00027; and of the sulphates of sodium, calcium, magnesium, aluminium, and iron, 0·001. H. Grunert studied this subject. J. Kolb examined the effect of foreign gases on the sp. gr. of sulphuric acid; and J. R. Pound, the sp. gr. of mixtures of ether and sulphuric acid.

The **molecular volumes** of sulphuric acid per gram-equivalent in l litres of water at 6°, given by F. Kohlrausch, were:

l . .	0·0002	0·002	0·01	0·05	0·1	1	5
Mol. vol. .	6·1	5·9	7·71	10·75	12·03	15·54	17·57

S. Sugden discussed the mol. vol. W. Grunert found the sp. gr. of mixtures of sulphuric acid and ammonium sulphate increase proportionally with the amount of salt added over the whole range examined at 20°, 40°, 60°, and 80°. The sp. gr. of soln. of the sulphates was discussed by J. G. McGregor, P. A. Favre and C. A. Valson, and L. F. Nilson and O. Pettersson; the mol. vol., by G. N. Wyrouboff, W. W. J. Nicol, J. H. Long, T. E. Thorpe and J. I. Watts, J. W. Retgers, A. E. H. Tutton, and L. F. Nilson and O. Pettersson; and H. Schröder, the vol. relations of the sulphites, chromates, and selenates, and the so-called **density modulus** of the sulphates, by C. A. Valson, C. Bender, J. Wagner, and J. C. G. de Marignac. N. S. Kurnakoff discussed the spatial relations of the atoms in sulphuric acid. J. Geissler gave for the ionic volume of HSO_4', 12·1.

The **contraction** which occurs when sulphuric acid is diluted with water was found by A. Ure to reach a maximum with the formation of $H_2SO_4.2H_2O$—73·13 per cent. H_2SO_4. Analogous observations were made by C. Langberg. J. L. Gay Lussac, G. T. Gerlach, J. R. Pound, E. B. H. Wade, J. N. Rakshit, H. Kopp, J. Kolb, G. Lunge, J. P. Rogers, and P. T. Meissner made observations on this subject. A. Bineau stated that at 0° the greatest contraction occurs with 75·5 per cent. H_2SO_4. D. I. Mendeléeff said that the relative position of the maximum does not change as the temp. rises from 0° to 400° although the actual magnitude alters; but S. U. Pickering, in agreement with J. Domke and W. Bein, found that the maximum is displaced by a change of temp. S. U. Pickering gave 67·0 per cent. H_2SO_4 at 8°; 67·5 per cent. at 17·9°; 69·1 per cent. at 28·1°; and 70·1 per cent. at 38·2°. J. Domke and W. Bein's results at 10° are plotted in Fig. 82. The following is a selection from the data for the contraction, C c.c., on mixing sulphuric acid with water to furnish a litre of soln. containing p per cent. H_2SO_4.

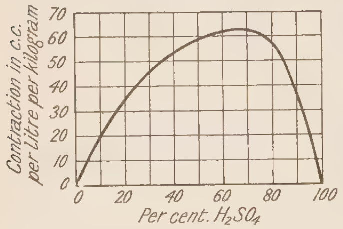

FIG. 82.—Contraction of Mixtures of Water and Sulphuric Acid.

p .	1	10	20	40	60	**67**	70	80	90	99
C .	2·4	19·0	34·3	53·0	61·6	**62·49**	62·4	58·7	40·8	5·6

Observations were also made by R. Kremann and R. Ehrlich, and J. N. Rakshit. K. Dieterici measured the contraction which occurs with very dil. soln. J. A. Wanklyn and J. Robinson found that if 100 c.c. of water and 200 c.c. of sulphuric acid be mixed in a 300 c.c. flask, the contractions, C c.c., corresponding with p per cent. H_2SO_4 are:

p . .	86	88	90	92	94	96	98
C . .	10·4	12·0	13·9	16·1	18·5	21·2	24·1

and they suggested determining the conc. of a given specimen of sulphuric acid from the contraction which occurs on mixing these volumes of acid and water. G. A. Haegmann made some speculations on what he called the *Kontraktionsenergiezahl*. According to J. Holmes and P. J. Sageman, the expansion which occurs on mixing soln. of sulphuric acid and various sulphates so as to yield 100 mols of acid and salt are represented by Fig. 83. The results are taken to be due to the action of physical forces, and independent of the action of chemical affinity or the formation of hydrosulphates. The sulphates of potassium, sodium, ammonium, copper, magnesium, and zinc are assumed to be aggregated in soln. The maximum with aluminium sulphate occurs with a mixture $Al_2(SO_4)_3.2H_2SO_4$, so that if aluminium sulphate is $Al_2(SO_4)_3$, the mol. of sulphuric acid is $(H_2SO_4)_2$. Observations were also made by G. Montemartini and L. Losana.

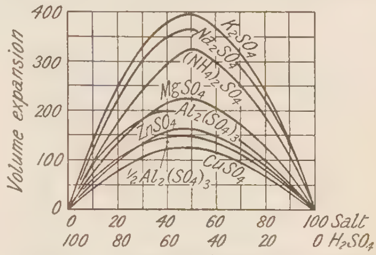

FIG. 83.—Volume Changes on Mixing Solutions of Sulphuric Acid and Sulphates.

T. Graham[3] found that when water is added to conc. sulphuric acid, the **viscosity** of the liquid increases to a maximum—corresponding with $H_2SO_4.H_2O$—and then decreases; and, added R. F. d'Arcy, this applies only for temp. up to 65°, for, at higher temp., the viscosity decreases continuously with increasing proportions of water. The phenomenon was attributed to the formation of hydrates in soln. R. Knietsch found that the speeds of outflow of fuming sulphuric acid at 23° when referred to water 100, for soln. of H_2SO_4 containing p per cent. SO_3, are:

p .	0·9	4·2	15·1	30·3	49·9	58·6	69·5	89·1	98·9
Time	145·7	147·0	151·0	166·9	198·7	192·0	145·0	109·9	100·7

For 100 per cent. H_2SO_4, at 0°, 33°, and 63·5°, R. Kremann and R. Ehrlich gave for the viscosity η=0·618, 0·172, and 0·076 respectively; T. Graham, η=0·2193 at 20°; F. Bergius, η=0·1915 at 25°; J. L. M. Poiseuille, η=0·3195 at 11·2°; J. R. Pound, η=0·210 at 30°. For N-, $0·5N$-, $0·25N$-, and $0·125N$-soln. of sulphuric acid at 25°, J. Wagner found the sp. viscosities (water unity) to be respectively 1·0898, 1·0433, 1·0216, and 1·0082. The results of A. E. Dunstan, and K. Drucker and R. Kassel (marked with an asterisk) are:

	0°	13·8°	15·0°	25°	50°	70°	76·5°	90°
η .	0·4843*	0·360	0·2694*	0·235	0·106	0·0635	0·0503*	0·0425

J. R. Pound gave for the soln. with p per cent. H_2SO_4, at 30°,

p .	99·924	95·723	93·410	85·070	80·243	58·356	26·492	0
η .	0·2134	0·1674	0·1691	0·1905	0·1568	0·0414	0·01426	0·0077

A. E. Dunstan and R. W. Wilson gave the following results at 25° as corrected by A. E. Dunstan:

p .	99·924	95·723	90·437	85·070	82·580	67·209	43·234	15·699
η .	0·24682	0·193567	0·20578	0·22040	0·20888	0·07515	0·02626	0·0136

There is a minimum for the 95 per cent. acid corresponding with $3H_2SO_4.H_2O$. The results are plotted in Fig. 84. S. B. Stone, A. Smits and co-workers, and F. H. Rhodes and C. B. Barbour made observations on this subject. A. E. Dunstan and R. W. Wilson also found that with soln. of p per cent. SO_3 in H_2SO_4 (water η=0·00474), at 60°:

p .	0	16·3	21·5	27·72	40·6	46·0	70·0
η .	0·0832	0·1383	0·1488	0·1753	0·2045	0·1791	0·1147

The sharp maximum corresponds with $H_2SO_4.SO_3$, and it agrees with the results of R. Knietsch's observations. W. Grunert found that the viscosity of mixtures of sulphuric acid and ammonium sulphate at 20°, 40°, 60°, and 80° increases slowly with the conc. of the acid until the conversion of the sulphate into hydrosulphate is completed, when the viscosity remains constant. J. L. R. Morgan and C. E. Davis found that when the viscosities are plotted with the deviations from the mixture rule, Fig. 84, the results agree with the existence of the hydrates $H_2SO_4.H_2O$, $3H_2SO_4.H_2O$, and 4 or $5H_2SO_4.H_2O$. J. Wagner, and H. Grunert investigated the viscosity of soln. of the sulphates. L. J. Simon found the viscosity of mixtures of sulphuric acid and sodium hydroxide gave a minimum corresponding with $NaHSO_4$; and with potassium and rubidium hydroxides, with K_2SO_4 and Rb_2SO_4 respectively; while H. Grunert found that an increased viscosity attends the formation of ammonium hydrosulphate. L. J. Simon measured the viscosity of mixtures of chromates and sulphates. J. R. Pound also measured the viscosity of mixtures of ether and sulphuric acid; K. Drucker and R. Kassel, mixtures of sulphuric and acetic acids; E. C. Bingham and S. B. Stone, mixtures of nitric and sulphuric acids; M. Bobtelsky and M. Janowskaja, mixtures of potassium and aluminium sulphates and sulphuric acid; and F. H. Rhodes and H. B. Hodge, mixtures of sulphuric and nitric acids.

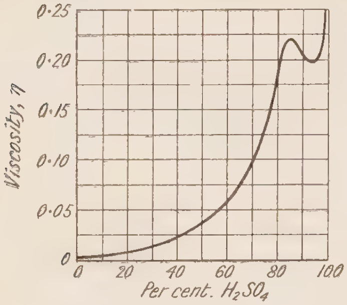

FIG. 84.—The Viscosity of Solutions of Sulphuric Acid at 25°.

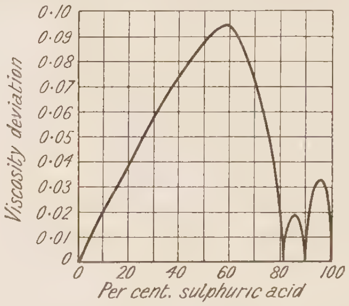

FIG. 85.—Viscosity-Deviations of Sulphuric Acid from Mixture Rule.

G. Meyer [4] found the **surface tension** in contact with mercury of sulphuric acid of sp. gr. 1·0559 to be $\sigma=316$ dynes per cm. at 20°; and M. Lenekewitz, for acids of sp. gr. 1·015 and 1·071, $\sigma=337·5$ and 319·7 dynes per cm. respectively at 19°–20°. Other observations were made by P. de Heen, P. Volkmann, A. Valson, G. Quincke, L. Grunmach, W. C. Röntgen and F. Schneider, C. Christiansen, W. H. Whatmough, etc. K. Ebeling gave the following values for the surface tension, σ dynes per cm., and the **specific cohesion,** a^2 sq. mm., at 18°, of sulphuric acid with p per cent. H_2SO_4, and in contact with air:

p	8·0	27·80	41·00	60·50	85·00
σ	73·58	76·13	77·80	76·52	67·61
a^2	14·25	12·87	12·08	10·13	6·76

C. E. Linebarger gave the following values for the surface tension, σ dynes per cm.:

Per cent. H_2SO_4	0°	10°	20°	30°	40°	50°	60°	70°
2·65	73·60	72·69	72·02	71·13	70·07	69·01	—	—
11·87	74·75	74·10	73·48	72·58	71·52	70·45	—	—
18·33	75·30	74·44	74·39	72·75	71·90	70·90	69·95	68·89
35·13	77·19	76·68	76·34	75·45	74·48	74·05	73·15	72·25
58·05	77·80	77·44	77·25	77·08	76·76	76·49	76·03	75·55
65·27	77·41	77·34	77·29	77·13	76·99	76·89	76·74	76·31
80·45	66·60	66·40	66·32	66·00	65·92	65·79	65·67	65·50
83·23	64·18	64·09	63·89	63·70	63·54	63·48	63·37	63·19
95·02	58·26	57·97	57·76	57·53	57·43	57·36	57·28	56·89

The results for 0°, 20°, and 50° are plotted in Fig. 86. With increasing proportions of sulphuric acid, the curves rise to a maximum when the proportion is nearly 60 per cent. H_2SO_4; thereafter, the surface tension falls with increasing proportions of H_2SO_4. The effect of temp. becomes less and less marked as the conc. of the acid increases. This is taken to mean that the molecules of the acid are polymerized to a high degree. J. L. R. Morgan and C. E. Davis measured the surface tension of soln. of the acid and found that when the results are plotted, Fig. 87, with the deviations from the mixture rule, there is a singular point corresponding with the hydrate $H_2SO_4.3H_2O$. G. Tammann, L. Abonnenc, and A. Smits and co-workers made observations on this subject. W. Herz and E. Knaebel measured the effect of ammonium and zinc sulphates on the surface tension. R. Knietsch measured the capillary rise, h mm., water 100, for sulphuric acid with p per cent. SO_3, at 22°, and found :

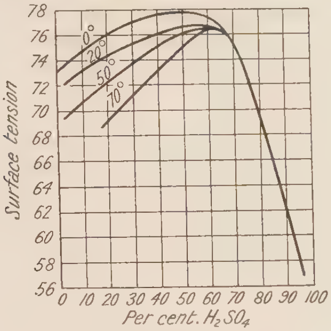

FIG. 86.—The Surface Tension of Sulphuric Acid.

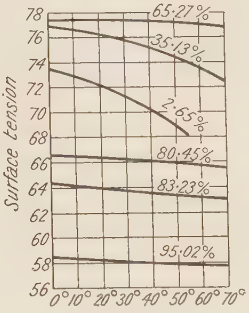

FIG. 87.—The Effect of Temperature on the Surface Tension of Sulphuric Acid.

p . .	0·9	4·2	15·1	30·3	49·9	69·5	89·1	98·9
h . .	38·23	38·23	37·64	36·47	35·29	29·41	24·70	23·52

F. Eötvös measured the molecular **surface energy** ; and E. Aston and W. Ramsay found for an acid of conc. $H_2SO_4+2H_2O$, at temp. :

	10·2°	46·4°	78·5°	132·5°	184·6°	237·7°	281·0°
σ . .	55·26	53·94	52·86	51·35	49·49	46·84	43·80
$\sigma(Mv)^{\frac{2}{3}}$.	787·6	778·8	772·5	763·8	749·7	724·9	690·1
$d\sigma(Mv)^{\frac{2}{3}}/d\theta$	0·209	0·209	0·209	0·297	0·599	1·072	
Association	32·3	32·3	32·3	19·1	6·7	2·8	

This corresponds with the formula $(H_2SO_4)_{32}$ for temp. below 132·5° ; and for temp. near 281°, $(H_2SO_4)_3$. W. Ramsay and J. Shields found that a soln. of constant boiling acid, $12H_2SO_4.H_2O$, gave mol. wts. for temp. ranging from 132·5° to 281°, from 32·3 times the normal value. This was taken to mean that the decrease in mol. wt. above 132·5° may be due either to a breaking up of the complex mols., or to a dissociation into sulphur trioxide and water. A. Christoff studied the effect of absorbed gases—hydrogen, oxygen, nitrogen, methane, and carbon monoxide—on the surface tension of sulphuric acid. J. R. Pound measured the surface tension of mixtures of sulphuric acid and ether ; and the interfacial tension of 42 organic liquids against sulphuric acid.

The rate of **diffusion** of sulphuric acid into water was measured by T. Graham,[5] who found that the rate of diffusion is more than half that of hydrochloric acid. The diffusivity with acids of different concentrations is fairly constant, but increases a little with the more conc. acid. J. J. Coleman found the speed to be slower than that of nitric or hydrochloric acid, or a soln. of potassium hydroxide, but faster than a soln. of ammonia, sodium hydroxide or chloride, or

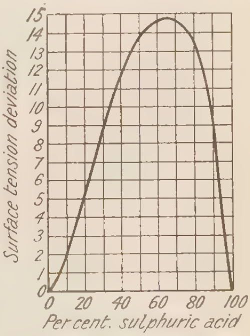

FIG. 88.—Surface Tension Deviations of Sulphuric Acid from the Mixture Rule.

magnesium sulphate. The rate of diffusion was measured by J. C. G. de Marignac, J. Stefan, and N. A. Umoff. G. Tammann examined the diffusion of sulphuric acid through a membrane of copper ferrocyanide against soln. of the alkali sulphates. Y. Terada measured the rate of dialysis. F. E. C. Scheffer gave for the rates of diffusion of soln. with 0·030, 0·162, 0·240, and 1·0N-H_2SO_4, respectively, k=1·04, 0·099, 1·02, and 1·07 gram-equivalents for sq. cm. per day at 7·5 to 8·5. G. Thovert gave for 18°,

N- . .	0·005	0·35	0·85	2·85	4·85	9·85
k . .	1·30	1·32	1·34	1·60	1·90	2·36

S. R. Carter and F. M. Lea studied the diffusion potentials at the boundaries involving hydrochloric and sulphuric acids and potassium chloride soln. While L. W. Oholm gave for 20° : 2N-soln., k=1·297 ; 1·5N-, k=1·350 ; N-, k=1·369 ; 0·5N-, k=1·399 ; and 0·1N-, k=1·498. F. Hinteregger, and J. C. G. de Marignac studied the rate of diffusion of soln. of the sulphates. P. de Heen calculated the radius of the **sphere of molecular action** of sulphuric acid to be 718×10^{-8} mm.

W. C. Röntgen and F. Schneider,[6] and O. Schmidt found the **compressibility** coefficient, β, of sulphuric acid, containing p per cent. H_2SO_4, to be, at 17·3° to 17·98°, and 8 atm. press. :

p . . .	6·57	12·7	35·76	47·58	62·37
β . . .	$0{\cdot}0_44458$	$0{\cdot}0_44246$	$0{\cdot}0_43386$	$0{\cdot}0_43189$	$0{\cdot}0_42917$

between 18·2° and 22° :

p .	7·0	20	31·1	44·7	63·0	72·0	91·7
β .	$0{\cdot}0_4431$	$0{\cdot}0_4365$	$0{\cdot}0_4314$	$0{\cdot}0_4276$	$0{\cdot}0_4242$	$0{\cdot}0_4228$	$0{\cdot}0_4250$

and for dT/dp, C. I. Burton and W. Marshall gave 0·0051. The subject was studied by G. Tammann. J. L. R. Morgan and C. E. Davis found that when the results are plotted, Fig. 89, with the deviations from the mixture rule, a singularity appears corresponding with the hydrate $H_2SO_4.H_2O$. J. H. Hildebrand gave 5300 atm. for the **internal pressure.**

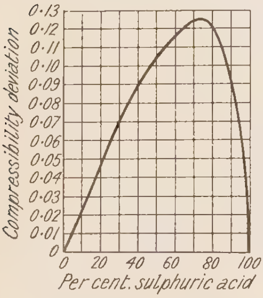

FIG. 89.—Compressibility Deviations of Sulphuric Acid from the Mixture Rule.

J. C. G. de Marignac[7] gave for the coeff. of **thermal expansion,** cubical, α, for $H_2SO_4.nH_2O$, when n=0, $\alpha=0{\cdot}0005758-0{\cdot}0_6864\theta$; n=5, $\alpha=0{\cdot}0005726-0{\cdot}0_6330\theta$; n=10, $\alpha=0{\cdot}0005858-0{\cdot}0_6367\theta$; n=15, $\alpha=0{\cdot}0005618-0{\cdot}0_6397\theta$; n=25, $\alpha=0{\cdot}0004625+0{\cdot}0_517752\theta$; n=50, $\alpha=0{\cdot}0002835+0{\cdot}0_551600\theta$; n=100, $\alpha=0{\cdot}0001450+0{\cdot}0_582860\theta$; n=200, $\alpha=0{\cdot}0000629+0{\cdot}0_598660\theta$; n=400, $\alpha=0{\cdot}0000333+0{\cdot}0_4100300\theta$. C. Forch found that for N-H_2SO_4, $\alpha=0{\cdot}0_5147$ from 0° to 5° ; $\alpha=0{\cdot}0_5196$ from 5° to 10° ; $\alpha=0{\cdot}0_5245$ from 10° to 15° ; $\alpha=0{\cdot}0_5287$ from 15° to 20° ; $\alpha=0{\cdot}0_5326$ from 20° to 25° ; $\alpha=0{\cdot}0_5361$ from 25° to 30° ; $\alpha=0{\cdot}0_5392$ from 30° to 35° ; and $\alpha=0{\cdot}0_5426$ from 35° to 40°. W. Kohlrausch gave for 96, 98, and 10 per cent. H_2SO_4, respectively $\alpha=0{\cdot}0_355$, $0{\cdot}0_355$, and $0{\cdot}0_357$. R. Kremann and R. Ehrlich found that the thermal expansion of mixtures of sulphuric acid and water has a well-defined maximum corresponding with $H_2SO_4.H_2O$; a dilation due to the dissociation of this hydrate is observed between 0° and 87·9°, and is greater at the lower temp., so that only a small proportion of this hydrate exists at 87·9°. Observations were also made by A. Bineau, G. Tammann, J. Kolb, G. Lunge, and A. Schertel ; while D. I. Mendeléeff, in accord with his theory of hydrate formation, worked out a number of maxima and minima values of α—*vide supra.* The thermal expansion of sulphuric acid has been also discussed in connection with the sp. gr.

According to H. F. Weber,[8] the **thermal conductivity** of sulphuric acid of sp. gr. 1·831 at 12°, is k=0·000765 cal. per cm. per sec. per degree ; G. Jaeger gave for 30, 60, and 90 per cent. H_2SO_4, at 32°, $k=0.001244$, 0·001047, and 0·000846 respectively; and C. Chree gave for sulphuric acid of sp. gr. 1·054, 1·10, 1·14, and 1·18, between 19·7° and 21°, $k=0.00126$, 0·00128, 0·00128, and 0·00130 respectively. W. von Beetz also made some observations on this property.

Observations on the **specific heat,** *c*, of sulphuric acid were made by L. Pfaundler,[9] J. Thomsen, J. C. G. de Marignac, F. Bode, G. Tammann, C. C. Person, etc. Results by E. Biron for sulphuric acid, $H_2SO_4.nH_2O$, or *p* per cent. H_2SO_4, are:

n .	0	0·2976	0·4856	0·9246	1·0	1·5439	2	3	5
p .	100	94·82	91·81	85·48	84·48	77·91	73·13	64·47	52·13
c .	0·3352	0·3554	0·3786	0·4345	0·4408	0·4517	0·4628	0·5012	0·5805

n .	6	7	10	13	16	20	50	200	1600
p .	47·57	43·75	35·23	29·52	25·39	21·38	9·82	2·65	0·3391
c .	0·6152	0·6475	0·7231	0·7717	0·8041	0·8339	0·9171	0·9763	0·9967

F. Bode gave:

Sp. gr. .	1·842	1·711	1·530	1·383	1·263	1·162	1·075	1·037
Sp. ht. .	0·3315	0·41	0·49	0·60	0·73	0·82	0·90	0·95

G. Agde and H. Holtmann gave for the sp. ht. of aq. soln. of sulphuric acid, between 25° and 45°:

H_2SO_4 .	1	10	20	40	60	80	100 per cent.
Sp. ht. .	0·990	0·918	0·839	0·680	0·535	0·424	0·338

The results are plotted in Fig. 90, where the dotted line represents values calculated by the additive rule. S. U. Pickering gave 0·2349 for solid H_2SO_4 at −30°, and 0·2721 at 0°; and for the liquid 0·345 at 20° and 0·358 at 50°; J. C. G. de Marignac gave 0·331 at 16°–20°, and 0·336 at 20°–56°; and C. Cattaneo, 0·332 at 5°–22°. For 50 per cent. H_2SO_4, C. Cattaneo gave 0·593, and for 5·2 per cent., 0·959 at 5°–22°; while J. C. G. de Marignac gave 0·975 for 2·2 per cent. H_2SO_4 at 16°–20°. H. Schlesinger gave for 65 per cent. H_2SO_4, 0·467, 0·443, and 0·458 respectively at 0°, 35°, and 70°; and for 85 per cent. H_2SO_4, 0·388 at 0° and 0·406 at 70°. L. Pfaundler gave the following values for the sp. ht., *c*, and the **molecular heat,** *C*, of H_2SO_4:

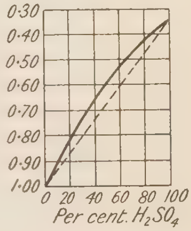

Fig. 90.—Specific Heat of Sulphuric Acid.

	22°–80°	81°–90°	91°–100°	101°–110°	111°–120°
Sp. ht. . .	0·355	0·356	0·358	0·359	0·360
Mol. ht. . .	34·790	34·888	35·084	35·182	35·280

	121°–130°	131°–140°	141°–150°	151°–160°	161°–170°
Sp. ht. . .	0·362	0·365	0·365	0·367	0·370
Mol. ht. . .	35·476	35·672	35·770	35·966	35·260

L. Pfaundler gave 0·470 for the sp. ht. of the dihydrate, $H_2SO_4.2H_2O$; and for the monohydrate, $H_2SO_4.H_2O$, 0·448. J. Thomsen, and J. C. G. de Marignac calculated the sp. ht. of a soln. containing nH_2O per mol. of H_2SO_4 from the formula $c(7{\cdot}3n)=2{\cdot}5+n$. M. Berthelot said that when a compound forms a hydrate in aq. soln., the thermal capacity diminishes, but E. Biron could not confirm this hypothesis in the case of sulphuric acid. R. Kremann and R. Ehrlich showed that the hydrate, $H_2SO_4.H_2O$, is stable only in the range of temp. between 0° and 130°. Hence, the sp. ht. of the mixture obtained by cooling from 130° should be greater than the sp. ht. determined by cooling from temp. above which the hydrate is completely decomposed. R. Kremann and F. Kerschbaum found evidence of this; they observed that the average sp. ht. of $H_2SO_4.H_2O$, between 33·7 and 207·1° is 0·430, and it increases slightly as the initial temp. rises; R. Auerbach gave 0·294 for the sp. ht. of liquid pyrosulphuric acid at 12°; and 0·154 for the solid acid. N. de Kolossowsky discussed the sp. ht. of the acid. R. Knietsch obtained the following values for the sp. ht., *c*, of fuming sulphuric acid containing *p* per cent. of free SO_3, at 35° :

p . .	2·0	12·89	23·78	34·67	51·00	72·78	89·12	100·0
c . .	0·345	0·340	0·340	0·350	0·370	0·495	0·650	0·77

J. R. Pound examined the sp. ht. of mixtures of ether and sulphuric acid.

G. Lunge,[10] J. Thilo, M. Altschul, E. Puchot, W. Hillmayr, R. Knietsch, E. Biron, R. Pictet, L. Pfaundler and E. Schnegg, S. U. Pickering, etc., made observations on the **freezing points,** and the **melting points** of binary mixtures of sulphur trioxide and water, in their bearing on the existence and properties of sulphuric acid and its hydrates. The data have been discussed in a special section —*vide supra*, Fig. 78. According to W. Ostwald, the f.p. of soln. of sulphuric acid shows that the acid is ionized in aq. soln. E. H. Loomis, S. U. Pickering, A. A. Noyes, and K. G. Falk, T. G. Bedford, W. Hillmayr, K. Drucker, A. Ponsot. H. Hausrath, M. Wildermann, M. Randall and G. N. Scott, T. S. Price, and H. C. Jones and co-workers measured the **molecular lowering of the freezing point,** and their results, if C denotes the number of grams of H_2SO_4 per 100 grms. of water ; $\theta°$, the f.p. ; C', mols of H_2SO_4 per 1000 grms. of water ; $\delta\theta$, the mol. lowerings of the f.p., are :

C .	0·00299	0·04095	0·1614	0·4520	1·056	4·360	14·712	24·520
θ .	−0·00161°	−0·02102°	−0·07569°	−0·1888°	−0·425°	−1·716°	−7·265°	−16·275°
C' .	0·000305	0·004175	0·01640	0·0461	0·1077	0·445	1·500	2·000
$\delta\theta$.	5·275°	5·03°	4·60°	4·10°	3·95°	3·86°	4·843°	6·510°

This means that the mol. wt. at first decreases rapidly as the concentration increases, reaches a minimum, and then rises again. H. C. Jones and co-workers showed that the results agree with the assumption that solvation occurs with soln. more conc. than $0·5N$-H_2SO_4—*vide supra,* the hydrates of sulphuric acid. E. Cornec found that the curve showing the lowering of the f.p. of sulphuric acid during its progressive neutralization with a soln. of potassium or ammonium hydroxide shows one break corresponding with the normal salt. F. M. Raoult determined the effect of sulphuric acid on the f.p. of ethylene bromide ; E. Mameli, acetic and chloracetic acids ; G. Ampola and E. Carlinfanti, nitrobenzene ; and G. Oddo, phosphoryl chloride. In nitrobenzene, acetic and chloracetic acids, formic acid, and in phosphoryl chloride, the computed mol. wt. agrees with $(H_2SO_4)_2$. F. M. Raoult discussed the mol. lowering of the f.p. of soln. of the sulphates. He found that the mol. wts. of freshly prepared soln. of sulphuric acid in acetic acid correspond with $(H_2SO_4)_2$, and that the molecules depolymerize on standing. G. Oddo and E. Scandola gave 6·81 for the **cryoscopic constant** of H_2SO_4 (f.p. 10·43°) ; R. Auerbach, 10·5° for pyrosulphuric acid ; and A. Hantzsch, 7·00 (with f.p. 10·46°). The mol. condition of various substances dissolved in absolute sulphuric acid were studied by G. Oddo and co-workers, and A. Hantzsch. R. Lespieau gave 4·8 for the cryoscopic constant of $H_2SO_4.H_2O$ (f.p. 8·4°) ; and he found the mol. lowering of the f.p. in liquid hydrogen cyanide to be 19·5.

J. L. Gay Lussac [11] said that when the vapour of sulphuric acid is passed through a white-hot porcelain tube, the sulphur trioxide is broken down into sulphur dioxide and oxygen, and H. St. C. Deville and H. Debray, and C. A. Winkler utilized the reaction for preparing oxygen. The acid was dropped into a red-hot retort filled with platinum scraps, or fragments of pottery ; the sulphur dioxide was removed by washing the mixed gases with water. According to T. B. Redwood, some sulphur dioxide is formed when sulphuric acid is distilled in a platinum retort. J. A. Wanklyn and J. Robinson showed that the vapour of sulphuric acid decomposes into sulphur trioxide and water, and the two gaseous components can be separated by atmolysis owing to their different rates of diffusion. M. Bodenstein and M. Katayama studied the **dissociation** of the vapour of sulphuric acid : $H_2SO_4 \rightleftharpoons H_2O+SO_3$, at temp. above 600°, and found that the dissociation constant, K, in $K[H_2SO_4]=[SO_3][H_2O]$, can be represented by $\log K=-Q/4·571T+0·75 \log T+4·086$, when the concentrations are expressed in mols per litre. The temp. of half dissociation at atm. press. is 623° K., when the calculated value is 599° K. By adding cT to the equation to allow for the difference in the sp. ht., c, of the substances formed and destroyed in the change, $\log K = -22850/4{\cdot}571T + 0{\cdot}75 \log T - 0{\cdot}00057T + 4{\cdot}086$, fits the observed results very well for acid vapour containing 85·05-100·5 per cent. H_2SO_4.

Observations on the **vapour pressure** of sulphuric acid in aq. soln. have been made by W. Müller-Erzbach,[12] M. Faillebin, K. Scheel, C. A. Perkins, T. Tate, R. von Helmholtz, F. L. Kortright, E. Aston and W. Ramsay, J. N. Brönsted, W. C. Ferguson, E. Baur, A. Vogel, W. Daudt, H. E. Roscoe, Lord Rayleigh, R. E. Wilson, and R. W. Gray and H. Whitaker. The results of H. V. Regnault are indicated in Table X for temp. ranging from 5° to 35°, and for conc. ranging from

TABLE X.—VAPOUR PRESSURES OF WATER OVER MIXTURES OF SULPHURIC ACID AND WATER (H. V. REGNAULT).

Temp.	Per cent. H_2SO_4 (Pressures in mm.)								
	84·48 $SO_3.2H_2O$	73·13 $SO_3.3H_2O$	64·47 $SO_3.4H_2O$	57·65 $SO_3.5H_2O$	52·13 $SO_3.6H_2O$	43·75 $SO_3.8H_2O$	37·69 $SO_3.10H_2O$	33·10 $SO_3.12H_2O$	24·26 $S_3.18H_2O$
5°	0·105	0·388	0·861	1·294	2·137	3·168	4·120	4·428	5·478
6°	0·106	0·409	0·922	1·399	2·296	3·398	4·416	4·787	5·879
7°	0·108	0·430	0·985	1·510	2·464	3·643	4·728	5·164	6·300
8°	0·110	0·452	1·053	1·628	2·641	3·902	5·059	5·562	6·745
9°	0·112	0·476	1·125	1·753	2·829	4·176	5·408	5·980	7·216
10°	0·115	0·501	1·200	1·885	3·029	4·466	5·777	6·420	7·712
11°	0·118	0·527	1·280	2·025	3·240	4·773	6·166	6·883	8·237
12°	0·121	0·556	1·364	2·173	3·463	5·098	6·578	7·371	8·790
13°	0·124	0·586	1·454	2·331	3·699	5·443	7·013	7·885	9·374
14°	0·127	0·617	1·548	2·498	3·950	5·808	7·473	8·425	9·991
15°	0·131	0·651	1·648	2·674	4·215	6·194	7·958	8·995	10·641
16°	0·135	0·687	1·753	2·861	4·495	6·603	8·471	9·592	11·329
17°	0·139	0·725	1·865	3·059	4·793	7·036	9·014	10·222	12·054
18°	0·144	0·765	1·983	3·270	5·107	7·495	9·586	10·885	12·820
19°	0·149	0·808	2·108	3·492	5·440	7·980	10·191	11·583	13·628
20°	0·154	0·853	2·241	3·728	5·792	8·494	10·831	12·317	14·482
21°	0·159	0·901	2·380	3·977	6·166	9·039	11·506	13·090	15·383
22°	0·165	0·952	2·528	4·243	6·561	9·615	12·220	13·904	16·334
23°	0·171	1·006	2·684	4·523	6·979	10·226	12·974	14·760	17·338
24°	0·177	1·064	2·849	4·820	7·422	10·872	13·771	15·661	18·397
25°	0·184	1·125	3·024	5·135	7·892	11·557	14·613	16·610	19·516
26°	0·191	1·190	3·209	5·469	8·388	12·282	15·503	17·608	20·697
27°	0·199	1·258	3·405	5·822	8·914	13·050	16·443	18·659	21·944
28°	0·207	1·331	3·611	6·197	9·471	13·862	17·436	19·765	23·260
29°	0·216	1·408	3·830	6·594	10·060	14·723	18·485	20·929	24·650
30°	0·225	1·490	4·061	7·014	10·684	15·635	19·594	22·154	26·117
31°	0·235	1·577	4·305	7·459	11·345	16·600	20·765	23·443	27·666
32°	0·245	1·670	4·564	7·933	12·045	17·622	22·003	24·800	29·300
33°	0·256	1·767	4·838	8·432	12·785	18·704	23·311	26·228	31·025
34°	0·256	1·871	5·127	8·962	13·569	19·850	24·692	27·732	32·847
35°	0·280	1·981	5·432	9·524	14·400	21·063	26·152	29·314	34·770

$SO_3.2H_2O$ to $SO_3.18H_2O$, or from 24·26 to 86·48 per cent. H_2SO_4. B. C. Burt gave for the vap. press., p mm., of water over mixtures of sulphuric acid and water—for 24·92 per cent. H_2SO_4:

	55°	60°	70°	75°	85°	95°	100°
p .	95·5	120·7	192·7	240·2	363·3	532·6	640·8

for 30·46 per cent. H_2SO_4:

	55°	60°	70°	75°	85°	95°	100°
p .	86·8	111·0	176·6	219·8	332·8	488·2	589·9

for 41·01 per cent. H_2SO_4 :

	60°	70°	80°	90°	100°	105°	110°
p .	84·2	136·5	211·8	317·2	465·8	560·2	670·2

for 54·24 per cent. H_2SO_4 :

	60°	70°	80°	90°	100°	115°	125°
p .	44·1	74·0	118·1	182·9	267·4	470·9	662·6

for 62·81 per cent. H_2SO_4 :

	70°	85°	95°	110°	120°	130°	140°
p .	35·4	73·6	115·8	210·8	308·0	438·3	612·8

for 70·78 per cent. H_2SO_4 :

	90°	100°	110°	120°	135°	150°	160°
p .	35·5	57·0	89·0	140·4	246·3	426·9	589·0

for 81·15 per cent. H_2SO_4 :

	135°	145°	150°	155°	160°	165°	170°
p .	52·8	82·6	101·7	124·6	150·4	180·9	218·9

for 91·01 per cent. H_2SO_4 :

	175°	185°	195°	205°	215°	220°	230°
p .	45·5	67·9	98·1	138·2	190·3	223·6	263·5

for 95·94 per cent. H_2SO_4 :

	205°	210°	215°	220°	225°	230°	235°
p .	34·1	40·8	50·1	60·8	72·2	85·9	106·0

B. C. Burt showed that the mol. wt. calculated from the vap. press. never rise above 32·7 and are usually below 32·7; they increase with temp., and decrease with greater concentrations. Inversion points frequently occur in the mol. wt.—temp. curves. It is therefore inferred that combination occurs in soln. forming new complexes, but there is no satisfactory evidence to show that definite hydrates exist in the soln. Using the data of B. Briggs in Table XI, and from those of E. Sorel in Table XII, A. W. Porter found that when E. Sorel's data are combined with J. Bertrand's vap. press. formula, and Clapeyron's equation, impossible values are obtained for the heats of soln. of sulphuric acid and water—*vide infra.* A. W. Porter represented B. C. Burt's results by $p=(1{\cdot}4455-1{\cdot}447T^{-1})^{50}$ for sulphuric acid; and R. Knietsch's results for fuming sulphuric acid by $p=(1{\cdot}295-94T^{-1})^{50}$ on the assumption that the mol. wt. of the vapour of sulphur trioxide is 80. C. H. Greenewalt compiled the following data for the constants a and b in the equation $\log p=a-bT^{-1}$ for soln. containing w per cent. H_2SO_4 :

w .	0	10	20	40	60	80	90	95
a . .	8·946	8·925	8·922	8·844	8·841	9·293	9·255	9·790
b . .	2260	2259	2268	2299	2458	3040	3390	3888

E. Knietsch measured the vap. press. of fuming sulphuric acid in an iron vessel three-quarters filled with the oleum, and the remainder with air. The manometer readings are indicated in Table XIII. J. W. McDavid also measured the vap. press. of fuming sulphuric acid. Observations on the **molecular lowering of the vapour pressure** of water, δ, by sulphuric acid were made by G. Tammann, A. Grollman and J. C. W. Frazer, M. C. Boswell and R. C. Cantelo, A. Smits, and C. Hacker. C. Dieterici found that at 0°, for soln. of normality N, the mol. lowerings of the vap. press. are :

N .	0·9505	0·4483	0·2323	0·1472	0·1106	0·0624
p_0-p .	0·1680	0·0767	0·0391	0·0246	0·0199	0·0105
. .	0·177	0·171	0·168	0·167	0·180	0·168

The results show that the mol. wt. increases with increasing concentration. A. Groll-

TABLE XI.—VAPOUR PRESSURE OF WATER OVER MIXTURES OF SULPHURIC ACID AND WATER (B. BRIGGS).

H_2SO_4 per cent.	Temperatures (Pressures in mm.)										
	100°	110°	120°	130°	140°	150°	160°	170°	180°	190°	200°
77·51	20·2	42·5	71·0	112·5	168·5	300·0	—	—	—	—	—
79·17	14·3	33·8	56·2	86·2	132·0	210·0	335·0	—	—	—	—
81·81	8·5	18·8	32·5	51·0	75·7	126·5	207·5	322·5	—	—	—
84·26	5·3	11·1	18·5	29·5	46·0	76·7	118·5	180·0	282·5	—	—
87·32	2·4	5·0	8·7	15·0	26·3	43·5	63·8	92·5	132·5	191·0	367
91·22	—	—	—	6·9	10·0	15·0	25·0	40·6	92·5	92·5	149

TABLE XII.—VAPOUR PRESSURE OF WATER OVER MIXTURES OF SULPHURIC ACID AND WATER (E. SOREL).

H_2SO_4 per cent.	Temperatures (Pressures in mm.)									
	10°	20°	30°	40°	50°	60°	70°	80°	90°	95°
44	4·4	8·5	15·5	28·1	48·3	—	—	—	—	—
46	4·0	7·7	14·5	26·3	44·4	76·5	—	—	—	—
48	3·7	7·1	13·4	23·9	40·1	69·0	107·2	—	—	—
50	3·3	6·5	12·0	21·4	35·9	61·3	95·6	152·0	236·7	—
52	3·0	5·8	10·9	18·9	31·5	54·0	84·5	131·2	207·9	251·5
54	2·6	5·0	9·5	16·5	27·8	47·2	74·8	116·1	183·5	222·0
56	2·2	4·3	8·1	14·2	24·1	41·6	65·0	100·9	160·0	195·0
58	1·9	3·5	7·2	12·0	20·4	34·5	55·4	86·2	138·5	169·5
60	1·6	3·0	6·1	10·0	16·9	28·7	46·1	72·3	118·7	146·0
62	1·4	2·6	5·0	8·1	13·9	23·9	37·7	59·7	100·7	125·0
64	1·2	2·2	4·0	6·5	10·9	18·7	30·3	48·0	83·7	105·0
66	1·1	1·8	3·5	5·4	8·9	15·2	24·2	39·0	70·0	88·0
68	0·9	1·5	3·0	4·5	7·2	12·3	19·4	31·4	56·0	72·0
70	0·8	1·3	2·5	3·8	5·9	9·5	15·5	25·5	44·4	57·0
72	0·7	1·0	2·0	3·2	4·8	7·5	12·0	20·0	33·7	43·4
74	0·5	0·6	1·7	2·6	3·9	6·0	9·5	15·4	24·5	31·5
76	0·4	0·5	1·4	2·1	3·0	4·8	7·5	11·8	18·5	22·0
78	0·3	0·4	1·1	1·7	2·4	3·5	5·7	8·5	13·0	15·8
80	0·2	0·3	0·8	1·3	1·9	2·9	4·1	6·2	9·3	11·0
82	0·1	0·2	0·5	0·9	1·4	2·0	2·7	3·9	5·6	6·8

TABLE XIII.—TOTAL VAPOUR PRESSURE OF FUMING SULPHURIC ACID.

Temp.	Per cent. oleum (Pressures in atmosphere).						
	30	40	50	60	70	80	100
35°	—	—	—	—	—	0·150	0·400
40°	—	0·075	—	0·225	0·375	0·500	0·650
50°	0·100	0·175	0·350	0·525	0·775	0·875	1·200
60°	0·200	0·275	0·550	0·825	1·400	1·500	1·850
70°	0·275	0·400	0·825	1·275	2·050	2·300	2·725
80°	0·400	0·575	1·150	1·850	3·100	3·500	4·000
90°	0·530	0·825	1·700	2·575	4·400	5·050	5·900
100°	0·730	1·100	2·400	3·700	6·000	—	—

man and J. C. W. Frazer also measured the lowering of the vap. press. of soln. up to $2·9M$-H_2SO_4. N. de Kolossowsky gave 5·35–5·95 for the **ebullioscopic constant.**

A. Bellani said that no sulphuric acid vapour is given off at ordinary temp., and T. Graham, that the dil. acid can be concentrated at a temp. not exceeding 190° without the loss of a particle of acid. G. A. Koenig, and A. Colefax stated that sulphuric acid is itself slightly volatile at temp. below 30°; and H. C. Gore also said that in vacuum desiccators sulphuric acid may lose 0·00656 mgrm. per sq. cm. per day owing to its volatility; but G. S. Johnson showed that the acid is not volatile at ordinary temp. even in a good vacuum, if no reducing vapours are present. H. Rebenstorff's statement that conc. sulphuric acid evaporates very slowly in dry air, but more quickly in moist air, has not been confirmed; and the same thing applies to P. M. Delacharlonny's statement that conc. sulphuric acid at 65°–70° gives off acid fumes. At higher temp., as shown by H. N. Morris, the acid may give off white fumes—*vide infra,* chemical mist. F. Krauss also said that a volatile compound is formed when barium sulphate is dissolved in conc. sulphuric acid. B. C. Burt's observations show that the observed vap. press. up to 200° are in all probability due to water alone; but J. S. Thomas and A. G. Ramsay have shown that the partial press. of the sulphuric acid is measurable at 140°, with 97·6 per cent. H_2SO_4; but with dil. acids the partial press. of H_2SO_4 is too small to measure accurately below 200°. The following is a selection from their results when the partial press. of the sulphuric acid vapour are expressed in mm. of mercury:

Per cent. H_2SO_4	160°	180°	200°	220°	230°	250°	260°
86·76	0·006	0·02	0·08	0·39	—	—	—
91·43	0·01	0·03	0·125	0·50	1·10	4·58	—
97·58	0·40	1·05	2·45	4·95	7·00	14·00	20·00
99·62	0·70	1·50	3·50	6·85	9·55	19·00	26·20

The results can be represented by $\log p=0·0145T-6·3258$, or $\log p=7·8315-3959T^{-1}$ for the 99·67 per cent. acid; by $\log p-0·0158T-7·1161$, or $\log p=8·5993-3899T^{-1}$ for the 97·58 per cent. acid; by $\log p=0·0317T-15·8923$, or $\log p=15·3259-8183T^{-1}$ for 91·43 per cent. acid; and by $\log p=0·0324T-16·4089$, or $\log p=17·7644-8967T^{-1}$ for the 86·76 per cent. acid. Where the press. are small, these relations are not reliable—*vide infra.* The vapour is probably present in the more or less dissociated form $H_2SO_4 \rightleftharpoons SO_3+H_2O$. J. S. Thomas and W. F. Barker measured the partial press. of both the water and the sulphuric acid. Selecting a few numbers from their tables

					Assuming complete dissociation.		
Per cent. H_2SO_4	θ	$p_{H_2SO_4}$	p_{H_2O}	P	P'_{SO_3}	p_{H_2O}	P'
89·25	183·0°	0·5	78·8	79·3	0·1	79·2	79·3
	216·5°	2·1	233·1	235·2	2·1	234·6	236·7
	241·5°	5·3	414·8	420·1	5·3	417·2	422·5
91·26	191·0°	0·6	50·7	51·3	0·6	51·3	51·9
	242·5°	6·4	271·6	278·0	6·4	275·7	282·1
	262·5°	16·3	411·1	427·4	15·9	419·0	434·9
95·06	180·0°	2·1	10·1	12·2	2·1	12·2	14·3
	244·5°	19·9	120·1	140·0	19·4	136·4	155·8
	282·0°	52·6	350·2	402·8	49·2	376·5	425·7
98·06	204·0°	5·9	0·0	5·9	5·9	5·9	11·8
	249·0°	28·5	2·6	31·1	27·5	20·0	57·5
	295·0°	132·3	14·7	147·0	112·7	125·2	237·0
99·23	211·0°	33·2	—	33·2	33·2	33·2	66·4
	244·0°	84·1	—	84·1	84·1	84·1	168·2
	290·0°	381·5	—	381·5	381·5	381·5	763·0

The partial press. can be represented by an equation of the type $\log_{10} p=a-bT^{-1}c \log T$. For 89·25 per cent. H_2SO_4, $\log_{10} p_{H_2SO_4}=75·5303+8529·90T^{-1}+21·4609 \log T$; $\log_{10} p_{H_2O}=-32·5120+216·85T^{-1}-13·114 \log T$; and $\log_{10} P=-33·5235+155·653T^{-1}-13·443 \log T$. For 91·26 per cent. H_2SO_4, $\log_{10} P_{H_2SO_4}=48·2388+7026·67T^{-1}=12·4310 \log T$; $\log_{10} p_{H_2O}=65·2394+7354·24T^{-1}+17·8856 \log T$; and $\log_{10} P=66·8040+7483·28T^{-1}+18·3659 \log T$. For 95·06 per cent. H_2SO_4, $\log P_{H_2SO_4}=-106·5692-4828·25T^{-1}-36·2945 \log T$; $\log_{10} P_{H_2O}=22·4406+4541·0T^{-1}$ $4·2726 \log T$; and $\log P=8·4658$

$+3516{\cdot}97T^{-1}-0{\cdot}1707\log T$. For 98·06 per cent. H_2SO_4, $\log p_{H_2SO_4}=8{\cdot}2878=4319{\cdot}7T-0{\cdot}5166\log T$; $\log_{10}p_{H_2O}=20{\cdot}7109+5415{\cdot}31T^{-1}+3{\cdot}6353\log T$; and $\log_{10}P=10{\cdot}8170+4518{\cdot}21T^{-1}+0{\cdot}2571\log T$. For 99·23 per cent. H_2SO_4, $\log p=-20{\cdot}0946+1695{\cdot}86T^{-1}-9{\cdot}3427\log T$.

The isothermal curves are plotted in Figs. 91 to 93. With the curves for the total

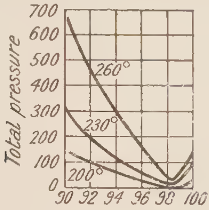

FIG. 91.—Total Vapour Pressure over Sulphuric Acid.

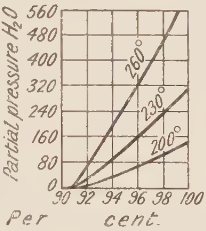

FIG. 92.—Partial Pressure of Water Vapour over Sulphuric Acid.

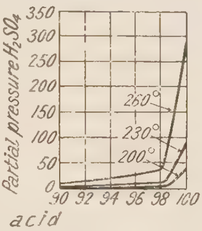

FIG. 93.—Partial Pressure of Acid over Sulphuric Acid.

press., and for the partial press. of H_2SO_4, there is an abrupt change of direction when the soln. contains 98·2 per cent. H_2SO_4. J. R. I. Hepburn, and I. R. McHaffie also measured the vap. press. of the water over 65·9–83·5 per cent. sulphuric acid between 15·5° and 17·5°, and the results agree with those of R. E. Wilson, and J. N. Brönsted. Formulæ proposed by P. Duhem,[13] M. Margules, J. von Zawidzky, and R. A. Lehfeldt, express the relationship between the composition of the liquid, and the partial vap. press. of its constituents. The results with the so-called Duhem-Margules' formula—**1**. 10, 10—are very fair in view of the complication arising from the dissociation of the acid. For the distillation of mixtures of sulphuric and nitric acids, *vide* nitric acid. A. Sanfourche and L. Rondier discussed the vap. press. of mixtures of sulphuric acid with nitrous and nitric acids. A. W. Porter, and J. R. Pound studied the vap. press. of mixtures of ether and sulphuric acid.

If a drop of sulphuric acid, H_2SO_4, be placed in a flask containing dust-free air, sat. with water vapour, a dense cloud appears. The **chemical mists** or *chemical fogs* produced by a reaction in the vaporous state—*e.g.* air containing ammonium chloride, phosphorus pentoxide, iodic acid, and sulphur dioxide—can be passed many times through water without the dissipation of the mist. H. N. Morris showed that the white fumes given off when conc. sulphuric acid is heated in a closed retort, are exceedingly difficult to absorb or condense. For instance, the white cloud persists after it has passed through a series of pipes immersed in water, and then through a coke scrubber moistened with water; after it has passed through water, dil. sulphuric acid, soda-lye, sodium carbonate soln., lime-water, ammonia, etc.; also through tubes packed with many of these solids. The sulphuric acid fumes were not visibly affected after passage through a 10 per cent. soln. of barium chloride, and the soln. becomes turbid only after 15 minutes' action. The cloud disappears after it has stood a long time in contact with water. The mists from chemical reactions were studied by H. Remy and co-workers. In the case of the burner gas of the contact process for sulphuric acid, the temp. is so high that the sulphuric acid must be dissociated into sulphur trioxide and water. It is not settled whether the two vapours on cooling form liquid sulphuric acid, or whether sulphuric acid vapour is formed and subsequently condensed. When the mist is formed, the vapours may condense on solid particles of dust, or on ionized gas molecules. The droplets are presumably larger the more slowly the gas is cooled, and R. Knietsch showed that with slow cooling the more readily the mist is clarified. It has been shown—**1**. 9, 6—that the smaller the droplets the greater the vap. press. As shown by J. S. E. Townsend, the vap. press. of the droplets may approach that of the water or dil. acid with which they are to be washed or scrubbed, so that the washing may be slow, and depend on the vigour of the mechanical agitation of gas and liquid. V. Rothmund's observations on these mists indicated that the mean diameter of the particles is 10^{-4} cm., and A. Delasalle obtained a similar value for the sulphuric acid mist. H. Remy found that the absorption of ammonium chloride mist is greater in water than in a nearly sat. soln. of that salt; with sulphuric acid mist, the absorption of water is visibly incomplete, whereas, with 98 per cent. sulphuric acid, the mist is cleared. Actually, however, the absorption by water is greatest, and the 98 per cent. acid is a bad solvent, but it renders the mist invisible—if the gas be then passed through water, the mist reappears. This is taken to mean that the sulphuric acid and sulphur trioxide mists must not be confused; the 98 per cent. sulphuric acid is the best absorbent for sulphur trioxide. The stability of the mists was discussed by W. E. Gibbs, S. Lehner and G. B. Taylor, E. Regener, H. O. Askew, and M. Pailly. Although the vap. press. increases as the droplets become smaller, an electric charge may act in the converse way. W. D. Bancroft said that the permanence of the mist may be due to a film of absorbed air on the surface of the particles, but E. Edser was unable to support the hypothesis. P. Pascal, and A. Delasalle discussed the electrostatic precipitation of sulphuric acid mist; and V. Kohlschütter, G. Nonhebel and co-workers, and A. Stäger, the properties of aërosols.

According to W. Beyerinck,[14] a drop of sulphuric acid, placed upon a glass plate, can absorb water vapour from its immediate neighbourhood, and thus surrounding itself with a sphere which is apparently free from moisture. The size of the sphere varies with the nature of the liquid taken; with sulphuric acid it is 2 or 3 cms. The size probably depends on the surface tension. The **desiccating power** of sulphuric acid of sp. gr. 1·838 is such that a litre of moist gas in contact with the acid retains $0{\cdot}0_525$ grm. of moisture—*vide* **1**. 7, 2. The subject was investigated by R. Fresenius,[15] E. W. Morley, C. H. Greenewalt, J. H. Yoe, G. P. Baxter and R. D. Warren, J. W. Marden and V. Elliott, F. M. G. Johnson, etc. R. E. Wilson, and W. K. Lewis and W. H. McAdams studied the control of the humidity of atmosphere by soln. of sulphuric acid.

J. Dalton [16] gave a table of the **boiling point** of sulphuric acid, and G. Lunge also gave a table from which the following data have been selected:

H_2SO_4 .	95·3	84·3	73·9	64·3	50·3	41·5	27·6	15·8	8·5 per cent.
B.p. .	297°	228°	180°	151·5°	124°	115°	107°	103·5°	101·5°
Press. .	718·8	720·5	725·2	730·1	730·1	730·1	732·9	732·9	735·0

A. Bussy said that fuming sulphuric acid begins to boil at 40°–50°; and R. Knietsch gave for the b.p. of fuming sulphuric acid at 759 mm. press.:

Free SO_3	3·64	9·63	26·23	42·84	63·20	97·20
B.p. .	212°	170°	125°	92°	60°	43°

T. Graham said that when the dil. acid is heated, water alone is first given off, and no acid vapour is evolved until the liquid has the composition $H_2SO_4.2H_2O$. C. G. Gmelin, C. Julin, and H. Hess found that an acid of sp. gr. 1·8435 gives off dil. acid until the residue has a sp. gr. 1·85. As previously indicated, the most conc. acid obtained by boiling down the ordinary acid contains a quantity of water and is variously stated by J. C. G. de Marignac, L. Pfaundler and A. Pölt, A. Bineau, H. E. Roscoe, W. Dittmar, G. Lunge and P. Naef, etc., to have 97·86–99·0 per cent. of H_2SO_4. G. Lunge, and R. Knietsch agree that the concentration of the constant boiling acid is 98·3 per cent. H_2SO_4. W. Dittmar said that the composition approximates to J. C. G. de Marignac's value $H_2SO_4.1\frac{1}{12}H_2O$, even when the press. ranges from 30 to 314 mm., while L. Pfaundler and A. Pölt observed that if a current of dry air be passed through soln. of sulphuric acid of different concentrations, at a temp., $\theta°$, the percentage amount of the monohydrate formed is $100-0{\cdot}005\theta$. The b.p. of this acid given by R. Knietsch is 330°, and this is the so-called maximum b.p. An acid of less conc. than 98·3 per cent. H_2SO_4 gives off water or dil. sulphuric acid until the b.p. 330° is attained; and an acid of greater conc. gives off sulphur trioxide until it has the constant boiling composition. The vap. press. of this acid in vacuo is immeasurably small. When sulphuric acid, below 80–82 per cent. H_2SO_4, is heated it gives off water vapour alone, or an inappreciable amount of sulphuric acid. J. S. Thomas and A. G. Ramsay showed that the partial vap. press. of sulphuric acid with soln. containing less than 92 per cent. H_2SO_4 is very small, but increases in magnitude with more conc. acids.

The **bumping** of the boiling acid has been discussed in connection with its concentration—*vide supra*. P. Vaillant studied the rate of evaporation of soln. of sulphuric acid. E. Beckmann gave 5·33 for the **ebullioscopic constant** of H_2SO_4 of b.p. 331·7°.

G. Oddo and E. Scandola,[17] S. U. Pickering, and A. Hantzsch, gave 24·03 cals. per gram, or 2·358 Cals. per mol for the latent **heat of fusion** of sulphuric acid, H_2SO_4, at about 10°; and R. Knietsch, 22·82 cals. per gram or 2·239 Cals. per mol. M. Berthelot gave 3·68 Cals. per mol or 31·72 cals. per gram for the heat of fusion of the monohydrate, $H_2SO_4.H_2O$; H. Hammerl gave 4·05–4·18 Cals.; S. U. Pickering, 4·63 Cals.; W. F. Luginin and G. Dupont gave for pyrosulphuric acid, 15·4 cals. per gram at 21°; and for sulphuric acid, 4·52 Cals.; while J. N. Brönsted gave 4·45 Cals. at about 8°. A. W. Porter calculated from R. Knietsch's observations the latent heats of fusion for fuming sulphuric acid with p per cent. of SO_3:

p . .	90	92	94	96	98	100
Heat fusion	25	26	24	25	23	22

E. Beckmann, and C. C. Person found the **heat of vaporization** of sulphuric acid, H_2SO_4, to be 122·1 cals. per gram, or 11·98 Cals. per mol at 326°. J. S. Thomas and A. G. Ramsay found that the heat of vaporization increases by dilution with acid; and that of water decreases; while below 220°, the latent heat of vaporization is fairly constant, but above that temp. it increases slowly with rise of temp. Thus, the heat of vaporization of sulphuric acid in Cals. per mol is:

Per cent. H_2SO_4	200°	210°	220°	230°	240°
99·62 .	18·00	16·84	16·25	15·93	16·07
97·58 .	18·19	16·88	16·57	16·20	16·22
91·43 .	—	37·38	33·55	—	—

The high values are due to heat effects attending the dissociation of the acid for the mol. latent heat (16,500 cals.) is compounded of the heat of evaporation of a mol of H_2SO_4 (16,100 cals.) plus the heat of formation of p/P mols of SO_3 (0·045×26600 cals.) less the heat of vaporization of p/P mols of water from the liquid (0·045×18000) cals. M. S. Vrevsky found the latent heat of vaporization of 53·07 per cent. sulphuric acid at 96·5° is 595·1 cals., when that of water at 79·3° is 552·4 cals. M. S. Vrevsky and P. B. Nikolsky found the difference in the latent heats of vaporization of water and 17 per cent. sulphuric acid is 1·2 cals.; between water and 57 per cent. sulphuric acid, 62·6 cals. If n denotes the number of mols of water per gram of acid; l, the latent heat of the acid; and l_0, the latent heat of water; then if $n>7·3$, $l=l_0\times1268n^{-2}$, and if $n<7·3$, $l=l_0\times62n^{-1}\times793n^{-2}$; and $(\delta Q/\delta n)n^2-(\delta Q/\delta n)n=RT\log_e(p_1/p_2)$.

According to A. W. Porter, the latent heat of evaporation, L, of the solvent of a soln. is obtained by adding the true heat of dilution, Q_d, to the latent heat of evaporation of the pure solvent $L_{\text{solvent}}\times Q_d$; and hence, at 15°, for soln. with p per cent. of SO_3:

p .	20	50	55	60	70	75	80
L .	595	659	687	724	844	945	1088 cals. per gram

J. Bertrand's equation $p=(a-bT^{-1})^n$, where a, b, and n are constants, and p denotes the vap. press. of water from the soln., the latter equation becomes $p=(1·4455\ -114·7T^{-1})^{50}$. Combining this result with Clapeyron's equation

$L = T(u-v)dp/dT$ from **1**. 9, 4, it follows that $L = 50R_p{}^{-0·02}$, where R is the gas constant. Hence, $L = 632·5p^{-0·02}$ cals. per gram. The latent heat of evaporation of a gram of water from a soln. of sulphuric acid :

Per cent. SO_3	15°	100°	150°	200°
20	595	545	510	467
50	659	612	579	538
60	724	681	650	611
70	844	810	784	750
80	1088	1077	1064	1044

The latent heat for the total evaporation of water from dil. sulphuric acid :

Per cent. SO_3	15°	100°	150°	200°
20	2832	2696	2591	2455
50	1008	1016	1005	1108
60	779	801	811	815
70	595	627	643	656
80	426	463	482	500

For the evaporation of sulphur trioxide from the fuming acid, J. Bertrand's formula becomes $p = (1·295 - 94T^{-1})^{50}$, and from Clapeyron's equation, the latent heat of evaporation of liquid trioxide becomes $L_s = 116·6p^{-0·02}$, when the mol. wt. of the vapour of sulphur trioxide is 80. The heat of total evaporation or condensation of sulphur trioxide :

Per cent. SO_3	0°	50°	100°	150°
80	1·599	1·684	1·790	1·891
85	1·903	2·023	2·156	2·296
90	2·400	2·548	2·717	2·898
95	3·816	3·958	4·145	4·357
98	7·632	7·606	7·695	7·849

From Clapeyron's equation, and R. Knietsch's vap. press. determinations, the latent heat of evaporation, of a gram of sulphur trioxide, as well as the values of a and b which fit J. Bertrand's equation $p = (a - bT^{-1})^{50}$ are :

Per cent. SO_3	a	b	40°	50°	60°	70°	80°	90°	100°
87·15	1·2082	80·0	—	—	102·5	101·9	101·1	100·5	99·9
89·00	1·2440	90·0	—	115·6	114·6	113·8	113·0	112·1	—
90·80	1·2464	92·0	—	116·6	115·6	114·6	113·9	113·0	112·2
92·65	1·2800	94·5	—	118·8	117·8	116·7	115·9	115·1	114·2
94·50	1·2890	94·0	—	—	115·8	114·9	114·0	113·2	112·5
96·30	1·3240	105·6	132·8	131·4	130·0	128·8	127·8	126·9	—
100·00	1·2950	94·0	117·0	116·2	115·3	114·4	113·5	112·6	—

Excepting the 87·15 and 96·30 per cent. soln., the latent heats are virtually the same. This would imply that the heat of dilution is zero or else R. Knietsch's data are not unimpeachable.

For the **heat of formation**, (SO_2,O,H_2O), J. Thomsen[18] gave 53·502 Cals., and M. Berthelot, 54·4 Cals. ; for (SO_2,O_2H_2), J. Thomsen gave 121·84 Cals. ; for (SO_3,H_2O), J. Thomsen gave 21·32 Cals., and M. Berthelot, 21·92 Cals. ; for $(S,3O,H_2O)$, J. Thomsen gave 124·574 Cals., and M. Berthelot, 124·00–133·0 Cals. ; and for $(S,2O_2,H_2)$, J. Thomsen gave 192·91 Cals., and M. Berthelot, 193·00–202·0 Cals. For the monohydrate, (H_2SO_4,H_2O), all solid, M. Berthelot gave 7·5 Cals., and S. U. Pickering, 6·533 Cals. ; if all liquid, M. Berthelot gave 6·12 Cals., J. Thomsen, 6·272 Cals., P. A. Favre and C. du Quaillard, 6·507 Cals., L. Pfaundler, 6·75572 Cals., and S. U. Pickering, 6·667 Cals. ; and if the initial products are liquid, and the final product solid, M. Berthelot gave 9·0 Cals. For the dihydrate, $(H_2SO_4,2H_2O)$, all liquid, P. A. Favre and C. du Quaillard gave 9·751 Cals., J. Thomsen, 9·364 Cals., and L. Pfaundler, 9·99796 Cals. For the trihydrate, $(H_2SO_4,3H_2O)$, all liquid, J. Thomsen gave 11·108 Cals., L. Pfaundler, 11·7845 Cals., and P. A. Favre and C. du Quaillard, 11·593 Cals. It will be observed that while the fixation of one mol of water to sulphur trioxide involves the evolution of 21·3 Cals., that of the second mol of water involves the evolution of 6·4 Cals., and that of the third mol, only 3·0 Cals. For the heat of formation of dil. sulphuric acid, (H_2SO_4,Aq.), J. Thomsen gave 17·848–17·850 Cals., and M. Berthelot, 17·00 Cals.; for (SO_3,Aq.), J. Thomsen gave 39·170 Cals., and M. Berthelot, 37·40 Cals., for (SO_{2gas},O,Aq.), J. Thomsen gave 71·332–71·350 Cals., and M. Berthelot, 72·00 Cals.; for (SO_2,Aq.,O), J. Thomsen gave 63·634 Cals., and M. Berthelot, 64·30 Cals., for (S,O_3,Aq.), J. Thomsen gave 142·404 Cals., and M. Berthelot, 141·00 Cals.; and for (S,$2O_2$,H_2,Aq.), J. Thomsen gave 210·76 Cals. M. Berthelot said that 47 Cals. are liberated for each atom of oxygen. G. N. Lewis and M. Randall estimated the **free energy** of the sulphate ion in *M*-soln. to be —176,500 cals. at 25°, and D. F. Smith and J. E. Mayer obtained —176,540 cals., while the free energy of 5·441*M*-H_2SO_4 is 169,850 cals. at 80° and —175,010 cals. at 25°. H. S. Harned and R. D. Sturgis studied this subject.

The mixing of conc. sulphuric acid with water is attended by the development of much heat. F. Göbel noticed that when sulphuric acid is poured into water in successive portions, rapidly following one another, without stirring, phosphorescence is sometimes produced which lasts for some seconds. J. J. Berzelius, and H. Hess observed that if sulphuric acid be mixed with one-fourth its weight of water, the temp. rises from 0° to 100°. Hence, water contained in a bulb, immersed in a flask in which the acid and water are mixed, will boil. J. Thomsen said the maximum rise of temp. 159° occurs when a mol of H_2SO_4 is mixed with a mol of water, or when one part by weight of the acid with 0·338 part of water. According to D. I. Mendeléeff, the maximum amount of heat is developed when the proportion of water corresponds with the dihydrate, $H_2SO_4+2H_2O$. He observed no exact proportionality between the quantity of heat developed and the contraction. M. Berthelot denied the statement of E. J. Maumené that there is any difference in the heat of soln. of freshly prepared and aged sulphuric acid. R. Knietsch found from the smoothed curve that the **heat of solution,** *Q* Cals., fuming sulphuric acid, containing *p* per cent. of SO_3, is for liquid and solid:

p	80	82	86	88	90	92	94	96	98	100
Liquid	178	199	250	278	308	344	381	421	465	515
Solid	—	—	—	—	286	322	360	402	442	486

A. W. Porter showed that R. Knietsch's results agree better with

Liquid	165	195	255	285	317	349	382	419	459	504
Solid	—	—	—	—	296	325	359	395	437	482

The heats of soln. or dilution, *Q* Cals., of a mol of H_2SO_4 with *n* mols of water were measured by J. Thomsen, P. A. Favre and J. T. Silbermann, T. Graham, H. Hess, J. J. B. Abria, J. C. G. de Marignac, P. A. Favre and C. du Quaillard, S. U. Pickering, G. Rümelin, H. von Steinwehr, L. Pfaundler, and J. N. Brönsted, and the results are indicated in Table XIV. J. A. Muller gave for the heat of dilution of a soln. with a mol H_2SO_4 per litre to infinite vol. 19·60 cals. at 14°; and M. Berthelot gave 10·06 Cals. for the heat developed by the soln. of a mol of crystalline H_2SO_4 in 50–100 parts of water, and for the liquid, 16·92 Cals. G. Rousseau and G. Tite said that the heat of soln. rises with temp. from 16·06 Cals. at 8° to 18·48 Cals. at 100°. J. Thomsen represented the heat, $Q_{H_2SO_4}$, evolved on mixing a mol of H_2SO_4 with *n* mols of water by the hyperbolic formula $Q_{H_2SO_4}=17860n/(n+1·798)$ cals.; and L. Pfaundler, $Q_{H_2SO_4}=17·920n/(n+0·001588)$ Cals. G. Rümelin found that the differential heat of soln. from J. Thomsen's expression, $dQ/dn=32150(n+1·798)^{-2}$ cals., is not reliable when *n* is greater than 10; and for values of *n* below 32 and above 10, he obtained better results with $dQ/dn=28120n^{-2}-558n^{-1}$ cals. There is here no reference to temp. M. Berthelot said that the change δQ in the quantity of heat developed on mixing H_2SO_4 with water at temp. θ_1 and θ_2 can be represented by $\delta Q=(c+c_1+c_2)(\theta_1-\theta_2)$, where c, c_1, and c_2 respectively denote the mol. sp. ht. of the components and of the mixture. M. Croullebois represented the quantity of heat *Q* liberated when *x* of water is added to a system containing x_0 of water, and the vap. press. of the water and soln. are respectively p and p_s, is $Q=L\int_{x_0}^{x}\{1-(p_s dp/d\theta)/(p dp_s/d\theta)\}$; but M. Berthelot questioned the accuracy of the result. If the above data be calculated to allow for the heat of formation of H_2SO_4 from SO_3 and H_2O, namely, 21·3 Cals., then the heats of dilution of sulphur trioxide, Q_{SO_3} Cals., with n mols of water, are:

n . .	1	1·5	2	2·5	3	5	1600
Q_{SO_3} .	21·30	25·01	28·04	30·03	21·31	34·14	40·34

and the data of J. Thomsen were represented by A. W. Porter to show the heat, Q_{SO_3} Cals. liberated when a gram of SO_3 is diluted with w grms. of water, $Q_{SO_3}=489{\cdot}2w/(w+0{\cdot}180)$ Cals., or from L. Pfaundler's and J. N. Brönsted's data, $Q_{SO_3}=504{\cdot}2w/(w+0{\cdot}2013)$ Cals. The differential coefficient of Q with respect to w represents the heat set free when a large amount of soln. containing a gram of SO_3 and w grms. of water is diluted with a gram of water. From the last expression, $dQ/dw=101{\cdot}5/(w+0{\cdot}2013)^2$. Expressing the data in terms of the percentage amount, p per cent., of SO_3 present in the final soln. containing a gram of SO_3, $Q_{SO_3}=504{\cdot}2(100-p)/(100-0{\cdot}7987p)$, or $dQ/dw=101{\cdot}5p^2/(100-0{\cdot}7987p)^2$. A. W. Porter represented the difference in the thermal capacity of soln. containing a gram of SO_3, before and after mixing, by $dN/d\theta=0{\cdot}714w/w+0{\cdot}062)$. Hence, the above expression for L. Pfaundler's and J. N. Brönsted's data applicable for temp. about 15°, assumes the form for any other temp., θ, and the heat of soln. of a gram of SO_3 in w grams of water at constant temp. is $Q_{SO_3}-504{\cdot}2w/(w+0{\cdot}2013)+0{\cdot}714w(\theta-15)/(w+0{\cdot}062)$; and the corresponding value for the differential heat of soln. is $dQ/dw=101{\cdot}5/(w+0{\cdot}2013)^2+0{\cdot}0443(\theta-15)/(w+0{\cdot}062)^2$. Transforming the expression for Q_{SO_3} to suit the case of W grms. of SO_3 in w grms. of water, at 0°, $WQ_{SO_3}=493{\cdot}5wW/(W+0{\cdot}2013W)+0{\cdot}714wW\theta/(w+0{\cdot}062W)$. The heat required to evaporate w grms. of water is WL, so that the quantity of heat required for the total evaporation of a soln. containing W grms. of SO_3 is $wL+WQ_{SO_3}$, meaning that this quantity of heat is set free when w grms. of water vapour condense at constant temp. into W grms. of SO_3 so as to produce sulphuric acid of the corre-

TABLE XIV.—HEATS OF SOLUTION OF H_2SO_4 IN WATER.

$n H_2O$	Per cent. H_2SO_4 in soln.	Cals. per mol. of H_2SO_4				
		L. Pfaundler, 11°	J. Thomsen, 20°	P. A. Favre, etc.	J. N. Brönsted, 16°	S. U. Pickering.
0·5	91·59	3·66618	—	3·544	3·750	3·706
1	84·48	6·77572	6·272	6·512	6·710	6·667
1·5	78·40	8·67986	—	8·354	8·790	—
2	73·13	9·99799	9·364	9·756	10·020	9·906
2·5	68·53	10·95542	—	—	—	—
3	64·47	11·78450	11·108	11·593	11·640	11·698
4	57·65	12·85760	—	12·750	12·830	12·902
5	52·13	13·56222	13·082	13·642	13·710	13·742
6	47·57	14·39522	—	14·396	14·370	14·407
7	43·75	—	—	15·008	14·890	—
8	40·49	—	—	15·474	15·260	—
9	37·69	—	14·952	—	15·580	15·675
19	22·28	—	16·256	—	—	16·916
49	10·00	—	16·684	—	—	17·361
99	5·21	—	16·858	—	17·600	17·610
199	2·66	—	17·065	—	17·760	17·748
399	1·34	—	17·313	—	18·120	18·073
799	0·67	—	17·641	—	18·506	18·560
1599	0·34	—	17·857	—	19·040	18·967
	0	17·920	17·994	—	—	—

sponding concentration; or the amount which would be required to re-evaporate this soln. and leave only SO_3 behind. In practice only differences of heat are required, namely, the difference corresponding with the evaporation from any stated concentration to any other attainable concentration. To dilute an infinite amount of soln. containing W grms. of SO_3 with an extra gram of water, heat is set free equal to $99{\cdot}33W^2/(w+0{\cdot}2013W)^2+0{\cdot}044W^2\theta/(w+0{\cdot}044W)^2$.

L. Pfaundler represented the heat, Q cals., evolved on mixing a mol of H_2SO_4 with a mol of

	$H_2SO_4.H_2O$	$H_2SO_4.2H_2O$	$H_2SO_4.3H_2O$	$H_2SO_4.4H_2O$	$H_2SO_4.5H_2O$
Q . .	0·708	3·528	5·614	7·365	8·252

of $H_2SO_4.H_2O$ with $H_2SO_4.2H_2O$, 0·272 Cal.; with $H_2SO_4.3H_2O$, 1·794 Cals; with $H_2SO_4.4H_2O$, 2·308 Cals.; and with $H_2SO_4.5H_2O$, 2·664 Cals.; of $H_2SO_4.2H_2O$ with H_2SO_4, 3·528 Cals.; with $H_2SO_4.H_2O$, 0·272 Cal.; with $H_2SO_4.3H_2O$, 0·266 Cal.; with $H_2SO_4.4H_2O$, 0·248 Cal.; and with $H_2SO_4.6H_2O$, 1·169 Cals.; and of $H_2SO_4.3H_2O$ with H_2SO_4, 5·614 Cals.; with $H_2SO_4.H_2O$, 1·794 Cals.; and with $H_2SO_4.2H_2O$, 0·266 Cal.

M. Berthelot gave for the heat of soln. of the solid monohydrate $H_2SO_4.H_2O$ $+400H_2O$, 7·12 Cals., and of the liquid, 10·80 Cals. J. Thomsen gave 11·58 Cals. for a mol of the liquid monohydrate and 1600 mols of water. R. Kremann and F. Kerschbaum showed that the heat developed on mixing sulphuric acid and water in equimolar parts is probably due to the process of soln. and not to the formation of the hydrate. D. P. Konowaloff gave 0·05949 Cals. per gram $H_2SO_4.H_2O$ for the heat developed when the monohydrate is diluted to $H_2SO_4.5H_2O$; and L. Pfaundler gave Q Cals. for the heat of dilution of a mol of $H_2SO_4.H_2O$ with n mols of water

n . .	1	2	3	4	5	∞
Q . .	3·305	4·815	6·077	6·966	7·680	10·921

For the heat of soln. of the dihydrate, $H_2SO_4.2H_2O$, with one mol of water, 1·510 Cals.; with 2 mols, 2·772 Cals.; with 3 mols, 3·661 Cals.; with 4 mols, 4·376 Cals.; and with an indefinitely large amount 7·617 Cals. For the heat of soln. of the trihydrate, $H_2SO_4.3H_2O$, with one mol of water, 1·262 Cals.; with 2 mols, 2·157 Cals.; with 3 mols, 2·866 Cals.; and with an indefinitely large amount, 6·106 Cals. M. Berthelot gave for the heat of soln. of a mol of small proportions of water H_2SO_4 with n mols of H_2O, 7·5 Cals. for $n=0{\cdot}05$; 7·25 Cals. for $n=0{\cdot}10$; 7·07 Cals. for $n=0{\cdot}15$; and 6·93 Cals. for $n=0{\cdot}20$. J. Thomsen found that the minimum heat is developed on mixing the acid with an amount of water equal to that already present. For $SO_3.nH_2O+nH_2O$:

n .	20	30	40	50	60	100	200	400	800
Q .	0·389	0·236	0·193	0·174	0·202	0·206	0·248	0·328	0·216

According to L. Pfaundler, the heat of soln. of $H_2SO_4.nH_2O$ with an excess of water is:

n .	0	0·5	1	1·5	2	2·5	3	4	5	6
Q .	17·754	13·984	10·921	9·133	7·617	6·729	6·106	4·844	3·955	3·241

He also observed that when $H_2SO_4.4H_2O$ is mixed with

	H_2O	$2H_2O$	∞H_2O	H_2SO_4	$H_2SO_4.H_2O$	$H_2SO_4.3H_2O$
Q .	0·889	1·603	4·844	7·365	2·308	0·248

and when $H_2SO_4.5H_2O$ is mixed with

	H_2O	∞H_2O	H_2SO_4	$H_2SO_4.H_2O$	$H_2SO_4.3H_2O$
Q . .	0·714	3·955	8·252	2·664	0·373

S. M. Naudé measured the heats of dilution of sulphuric acid; J. Thomsen, M. Berthelot, and P. A. Favre and C. A. Valson, the heats of soln. of various sulphates in water; and D. D. Karve, the heat of soln. of sulphuric acid in aq. and non-aq. solvents.

J. B. Richter observed that a mixture of equal parts of conc. sulphuric acid and snow evolves heat, but no change of temp. occurs with a 4 : 5 mixture, and with a larger proportion of snow, intense cold is produced by the **freezing mixture.** L. Pfaundler mixed sulphuric acid—$H_2SO_4+2·874H_2O$ or 66·19 per cent. H_2SO_4—with snow, so that a kilogram of the mixture, made at 0°, contained p per cent. of the given acid, and found that the temp. fell to θ_1°, and when all the snow had melted, it rose to θ_2°, whereby Q Cals. of heat were absorbed:

p . .	47·7	39·1	31·0	23·9	18·8	14·3	9·9	7·0
θ_1 . .	37°	−34°	−31°	−28°	−25°	−22°	−19°	−16°
θ_2 . .	37°	−21·5°	−14·5°	−9·5°	−7·0°	−3·9°	−2·8°	−2·1
Q .	0	18·4	33·2	43·0	51·3	58·2	69·3	68·6

According to M. Berthelot, a mixture of a mol of H_2SO_4 with 18 mols of H_2O as snow at 0° absorbs 8·5 Cals. and lowers the temp. to —28·7°. A mixture of 3 parts of snow with one of liquid H_2SO_4 mixed with one-fifth of its weight of water lowers the temp. to —32·5°, and if the constituents be first cooled to —7°, the temp. drops to —51°. He also found that the heat absorbed (—18·03 Cals.) when the monohydrate, $H_2SO_4.H_2O$, is mixed with snow is a resultant of the fusion of a mol of the monohydrate (—3·68 Cals.), the fusion of 17 mols of H_2O (—24·31 Cals.), and the union of a mol of the monohydrate with 17 mols of water (9·960 Cals.). Starting from 0°, the temp. drops to —52·6°; and for each degree below 0° at the start, the quantity of heat absorbed increases by $\frac{1}{110}$. J. I. Pierre and E. Puchot observed that by mixing 3 parts of the crystalline monohydrate with 8 parts of snow or pulverized ice, the temp. falls to —26·2°, and with the liquid acid, to —19·5°. I. A. Bachman found that 100 c.c. of a mixture of sulphuric and nitric acids with 340 grms. of snow or pulverized ice lowers the temp. 30°–32°.

For the **heat of neutralization** of a mol of lithium hydroxide with $\frac{1}{2}H_2SO_4$, R. Varet gave 15·654 Cals.; M. Berthelot gave for sodium hydroxide, 15·69–15·87 Cals.; potassium hydroxide, 15·645–15·7 Cals.; ammonium hydroxide, 14·075–14·5 Cals.; E. Petersen gave for thallium hydroxide, 15–65 Cals.; M. Berthelot for calcium hydroxide, 15·57 Cals.; strontium hydroxide, 15·355 Cals.; barium hydroxide, 18·45 Cals.; magnesium hydroxide, 15·1–15·61 Cals.; zinc hydroxide, 11·7–11·705 Cals.; cadmium hydroxide, 11·91 Cals.; manganese hydroxide, 13·24–13·5 Cals.; ferrous hydroxide, 12·46 Cals.; cobalt hydroxide, 12·336 Cals.; nickel hydroxide, 13·055 Cals.; cupric hydroxide, 9·22 Cals.; cupric oxide, 9·40 Cals.; silver oxide, 7·245 Cals.; lead monoxide, 11·69 Cals.; aluminium hydroxide, 10·495–10·57 Cals.; chromic hydroxide, 8·22 Cals.; and ferric hydroxide, 5·64–5·70 Cals.; R. Varet gave for mercurous oxide, 5·9 Cals.; and for mercuric oxide, 1·3 Cals.; and J. Aloy gave for uranyl hydroxide, $\frac{1}{2}UO_2(OH)_2$, 4·75 Cals. For mixtures of a mol of sulphuric acid in aq. soln. and 1, 2, and 4 mols of NaOH in aq. soln., M. Berthelot gave 14·754, 31·378, and 31·365 Cals. respectively; for 1 and 2 mols of KOH in aq. soln., 14·7 and 31·4 Cals. respectively; and for 1 and 2 mols of ammonium hydroxide in aq. soln., 13·6 and 29·05 Cals. respectively. P. Dutoit and E. Grobet measured the rise of temp. during the progressive neutralization of bases with sulphuric acid with the idea of detecting the formation of basic salts, etc. J. W. McDavid measured the heat developed on mixing sulphuric acid, nitric acid, and water.

B. Powell[19] first measured the **refractive index** of soln. of sulphuric acid and obtained $\mu=1·835$ for an acid approximating 94·5 per cent. H_2SO_4. V. S. M. van der Willigen observed that the index of refraction of sulphuric acid increases with the addition of water until a maximum is attained with $H_2SO_4.H_2O$. The results showed that the mixture formula: $(100-p)(\mu^2-1)/d+p(\mu_1^2-1)/d_1=(\mu_2^2-1)/d_2$, where p denotes the percentage amount of sulphuric acid, and μ, μ_1, and μ_2, and d, d_1, and d_2 denote the refractive indices and sp. gr. of sulphuric acid, water, and the mixture respectively, is not applicable. For dil. soln. the empirical formula

$\mu=a+bp+cp^2$ can be used. The coefficients of the standard dispersion formula $\mu=a+b\lambda^{-2}+c\lambda^{-4}$ show a marked change at about 72 per cent. H_2SO_4. The data were recalculated by the Kaiserlichen Normal-Eichungs Kommission, and by S. U. Pickering. The latter said that breaks in the curve occur corresponding with the hydrates 84·5 per cent. H_2SO_4, or $H_2SO_4.H_2O$; $H_2SO_4.4H_2O$ with 57·7 per cent. H_2SO_4, or with 24–30 per cent. H_2SO_4. C. Féry reported breaks corresponding with the hydrates $H_2SO_4 : H_2O=1 : 4, 1 : 2, 1 : 1\frac{1}{2}$, and $1 : 1$. R. Nasini gave for the index of refraction, μ, of sulphuric acid $H_2SO_4.\frac{1}{2}H_2O$, and sp. gr. 1·827, respectively 1·437, 1·434, 1·429, and 1·427 for the H_γ-, F-, D-, and C-lines B. Wagner gave for the D-line at 17·5° for soln. containing p per cent. H_2SO_4:

p . .	1	5	10	15	20	25	30
μ . .	1·33449	1·33912	1·34465	1·34999	1·35513	1·36007	1·36475

while for more conc. soln., V. F. Hess gave for sulphuric acid:

	p . .	0	19·981	39·757	59·980	80·096	100
	Sp. gr. .	0·99913	1·13814	1·29359	1·48032	1·69550	1·84167
μ	C-line .	1·33184	1·35588	1·37959	1·40429	1·42854	1·42564
	D-line .	1·33364	1·35782	1·38169	1·40653	1·43083	1·43772
	F-line .	1·33775	1·36223	1·38632	1·41139	1·43586	1·43226
	G'-line .	1·34100	1·36563	1·39002	1·41520	1·43958	1·43577

Observations were also made by W. Hallwachs, F. Kohlrausch and co-workers, W. Hallwachs, C. Chéneveau, K. Fajans and co-workers, J. Dinkhauser, M. le Blanc, A. Handl and A. Weiss, H. Kohner and M. L. Gressmann, and H. Becquerel. V. H. Veley and J. J. Manley obtained the results indicated in Table XV. V. H. Veley and J. J. Manley plot the results to show that the resulting curve can be resolved into half a dozen straight lines, but, as they remark, "the points of discontinuity are to some extent ideal, in that an apparently abrupt change of events can be resolved into a gradual transition stage." There is a well-defined maximum corresponding with H_2SO_4, and less well-marked points with the hydrates $H_2SO_4.H_2O$, and $H_2SO_4.2H_2O$. J. L. R. Morgan and C. E. Davis found that the indices of refraction observed by V. H. Veley and J. J. Manley when plotted, Fig. 94, to show deviations from the mixture law, gave a curve with breaks corresponding with the hydrates $H_2SO_4.H_2O$, and $H_2SO_4.2H_2O$. G. Rossi and A. Marescotti measured the index of refraction of sulphuric acid containing colloidal sulphur.

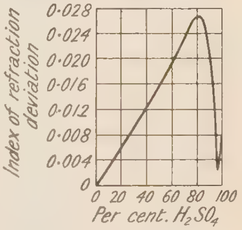

FIG. 94.—Index of Refraction Deviations of Sulphuric Acid from the Mixture Rule.

J. H. Gladstone calculated the **molecular refraction**, R, for soln. with p per cent. H_2SO_4, for the H_α-, D-, and H_β-lines:

	p . .	98·00	89·75	80·05	71·91	63·20	37·20	21·00	11·30	5·80
R	H_α- .	22·32	22·44	22·49	22·56	22·51	22·73	22·86	22·96	23·00
	D- .	22·47	22·55	22·61	22·66	22·65	22·80	22·96	22·94	22·75
	H_β- .	22·66	22·80	22·87	22·92	22·94	22·20	22·07	23·22	22·95

The refraction equivalents of J. H. Gladstone were calculated from the formula $(\mu-1)/d$=constant; but V. H. Veley and J. J. Manley calculated values from the $(\mu^2-1)/(\mu^2+2)d$=constant. They found that with soln. between 3 and 95 per cent. H_2SO_4, the sp. gr. is a complicated function of the concentration, yet the factor $(\mu^2-1)/(\mu^2+2)$ is a linear function of the density or "in other words, the ethereal elasticity is in simple direct relation to the density." W. J. Pope gave 17·08 for the refraction eq. of the SO_4-radicle. The subject was discussed by J. A. Wasastjerna, and A. Hantzsch and F. Dürigen. C. V. Raman said that the observations on the scattering of light by sulphuric acid indicate that the SO_4-ion is nearly isotropic. S. Venkateswaran, and C. W. Sweitzer discussed the scattering of light; and J. Moir, the colour of substances in sulphuric acid soln.; I. I. Kanonnikoff gave 16·84 for the refraction equivalent of the SO_4-radicle. C. V. Raman found that dust-free sulphuric acid almost completely polarizes the scattered light.

TABLE XV.—INDICES OF REFRACTION FOR SOLUTION OF SULPHURIC ACID.

Per cent. H_2SO_4	Indices of Refraction			
	H_α-line	D-line	H_β-line	H_γ-line
0·84	1·332805	1·334664	1·338807	1·342029
1·76	1·333944	1·335794	1·339984	1·343181
3·88	1·336416	1·338313	1·343490	1·345704
5·1	1·337896	1·339855	1·343964	1·347326
9·58	1·343485	1·345361	1·349633	1·352955
14·0	1·349001	1·350953	1·355233	1·358576
18·31	1·345322	1·356297	1·360653	1·363939
22·16	1·359194	1·361248	1·365598	1·368854
25·9	1·364051	1·366050	1·370506	1·373882
29·24	1·368110	1·370196	1·374726	1·378211
30·86	1·370161	1·372280	1·376830	1·380248
34·35	1·374213	1·376332	1·380948	1·384426
34·48	1·379184	1·381388	1·386002	1·389530
42·45	1·384119	1·386350	1·390090	1·394507
46·64	1·388987	1·391184	1·395934	1·399508
52·24	1·396336	1·398589	1·403405	1·406851
56·22	1·401655	1·403907	1·408767	1·412274
59·65	1·406267	1·408582	1·413445	1·416976
62·88	1·410536	1·412850	1·417767	1·421437
66·44	1·415487	1·417822	1·422782	1·426452
69·6	1·419838	1·422156	1·427177	1·430848
72·28	1·423549	1·425950	1·430943	1·434584
74·86	1·426858	1·429185	1·434234	1·437933
76·3	1·428767	1·431132	1·436185	1·439887
76·59	1·429030	1·431388	1·436494	1·440167
78·09	1·430841	1·433203	1·438242	1·441983
80·05	1·432946	1·435290	1·440335	1·444079
80·43	1·433230	1·435628	1·440658	1·444380
81·77	1·434442	1·436818	1·441871	1·445582
83·2	1·435459	1·437820	1·442875	1·446570
84·56	1·436051	1·438403	1·443417	1·447071
85·50	1·436267	1·438632	1·443603	1·447277
85·92	1·436272	1·438632	1·443651	1·447384
86·37	1·436246	1·438591	1·443570	1·447324
87·40	1·436065	1·438410	1·443410	1·447031
90·53	1·434180	1·436468	1·441361	1·449978
95·33	1·430862	1·433061	1·437836	1·441402
97·3	1·425367	1·427482	1·432064	1·435420
98·7	1·419470	1·421558	1·426025	1·429396
99·3	1·418387	1·420450	1·429845	1·428206

J. L. R. Morgan and R. H. Crist found the extinction coefficient—k in $l = l_0{}^{e-kd}$, or $k = \{\log (l_0/l)\}/d$, where d, the depth of the soln., is 2 cms.—for light of wave-length λ in $m\mu$:

	λ . . .	0·1	0·3	0·5	0·7	0·9	1·1	1·3	1·5
k	0·05M-soln. .	201	200	199	199	198	198	197	197
	5·00M-soln. .	221	207	203	200	200	200	200	200

V. S. M. van der Willigen found that the **absorption spectrum** of sulphuric acid attains a maximum with soln. containing 81·41 per cent. H_2SO_4. W. N. Hartley observed that a normal soln. of the acid, through a column of liquid 200 mm. long, exhibits a spectrum which is continuous to $\lambda^{-1} = 4413$, and but slightly enfeebled from this point to $\lambda^{-1} = 4555$; the same soln. in a 100 mm. column transmits a spectrum which is practically that of water. W. W. Coblentz found that the **ultra-**

red transmission spectrum of sulphuric acid, Fig. 95, shows no water bands. The opacity of the substance makes it difficult to decide on the SO_4 band at 4·5μ; there is a broad shallow band at 3·6μ. The bands at 6·2μ and 6·5μ may be due to SO_4; they were conspicuous in the many sulphate soln. which were examined and which also have a common band at 6·5μ. The **ultra-red reflection spectrum**, Fig. 95, has maxima at 8·6μ, 9·55μ, 10·42μ, and 11·35μ. The bands 8·6μ and 9·55μ occur both in hydrated and anhydrous sulphates, and are due to the SO_4-radicle. The 10·4μ band is due to SO_3. W. W. Coblentz, A. M. Taylor, K. Rolan, and R. Schachenmeier also studied both ultra-red spectra of a number of sulphates. C. Schaefer and M. Schubert found that the ultra-red reflection spectrum of the sulphates shows two well-developed maxima at about 9μ and 16μ. In the case of the isotropic sulphates (alums), the maximum at 9μ appears to correspond with a single frequency, although the employment of greater dispersion may disclose complex structure. For uniaxial crystals the maxima at both 9μ and 16μ show the existence of two characteristic frequencies, corresponding with the ordinary and extraordinary rays respectively. In the case of biaxial crystals the maximum at 9μ consists of three separate vibrations corresponding with the three refractive indices. It is probable that the structure of the maximum at 16μ is of the same type. The two selective frequencies which are shown by all the sulphates examined are obviously connected with the SO_4 group. The optical properties of the sulphates were studied by A. Arzruni, H. Reinsch, H. Töpsöe and C. Christiansen, A. E. H. Tutton, C. A. Valson, and G. N. Wyrouboff. A. M. Taylor, R. G. Dickinson and R. T. Dillon, and S. K. Mukherjee and P. N. Sengupta, and P. Pringsheim and M. Yost studied the **Raman effect** with sulphates; and S. J. Wawiloff and L. A. Tummermann, the **photoluminescence**.

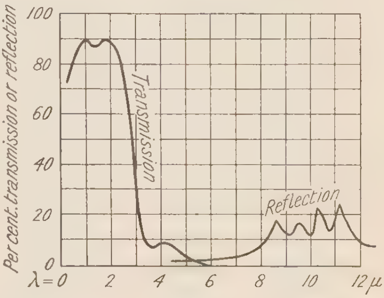

Fig. 95.—Ultra-red Transmission and Reflection Spectra of Sulphuric Acid.

The **magnetic-optic rotatory power** was measured by O. Wachsmuth,[20] and J. Forchheimer. W. H. Perkin found that for soln. with p per cent. H_2SO_4, at a temp. $\theta°$, the electromagnetic rotation of the plane of polarization, M, amounted to

p . .	9·179	47·41	47·41	73·00	93·66	99·92
θ . .	14·7°	15·6°	90·1°	16·9°	15·3°	17·1
M .	1·921	1·983	2·011	2·114	2·258	2·304

S. U. Pickering said that the results are in accord with the presence of the hydrates $H_2SO_4.H_2O$, and $H_2SO_4.4H_2O$. W. H. Perkin considered that his results were not in accord with the theory of ions, but J. Walker said that there is no contradiction if it be assumed that the increased conductivity with rise of temp. is due to the increased mobility of the ions.

A. Kailan [21] examined the effect of radium rays on sulphuric acid; H. Shiba and T. Watanabe, the X-ray diffraction; and T. Swensson, the change in the conductivity, etc., on exposure to light.

F. Kohlrausch [22] measured the **electrical conductivity** of sulphuric acid in aq. soln. at 18°, and his results are indicated in Table XVI. There is a maximum in the conductivity curve with 30 per cent. H_2SO_4; below this concentration the conductivity decreases as the concentration diminishes, and above this concentration, the conductivity slowly decreases as the concentration increases up to 84·5 per cent. H_2SO_4, corresponding with the monohydrate, $H_2SO_4.H_2O$. The conductivity slowly increases as the concentration increases above 84·5 per cent. until 92 per cent., above which the conductivity rapidly decreases to that of pure sulphuric acid.

TABLE XVI.—THE ELECTRICAL CONDUCTIVITIES OF AQUEOUS SOLUTIONS OF SULPHURIC ACID.

H_2SO_4 per cent.	$\eta \times 10^3$ grm. eq. per litre	Sp. gr.	K mhos $\times 10^4$.	Eq. conduct $\lambda = k/n$	Temp. coeff. 18°–26°
5	1·053	1·0331	2085	198·0	0·0121
10	2·176	1·0673	3915	179·9	0·0128
15	3·376	1·036	5432	160·9	0·0136
20	4·655	1·1414	6527	140·2	0·0145
25	6·019	1·1807	7171	119·2	0·0154
30	7·469	1·2207	7388	98·9	0·0162
35	9·011	1·2625	7243	80·4	0·0170
40	10·649	1·3056	6800	63·8	0·0178
45	12·376	1·3508	6164	49·7	0·0186
50	14·256	1·3984	5405	37·9	0·0193
55	16·248	1·4487	4576	28·16	0·0201
60	18·375	1·5019	3726	20·27	0·0213
65	20·177	1·5577	2905	14·40	0·0230
70	23·047	1·6146	2152	9·36	0·0256
75	25·592	1·6734	1522	5·95	0·0291
78	27·18	—	1238	4·55	0·0323
80	28·25	1·7320	1105	3·91	0·0349
81	28·78	—	1055	3·67	0·0359
82	29·31	—	1015	3·46	0·0365
83	29·84	—	989	3·32	0·0369
84	30·37	—	979	3·225	0·0369
85	30·90	1·7827	980	3·172	0·0365
86	31·41	—	992	3·161	0·0357
87	31·90	—	1010	3·169	0·0349
88	32·39	—	1033	3·193	0·0339
89	32·87	—	1055	3·212	0·0330
90	33·34	1·8167	1075	3·224	0·0320
91	33·80	—	1093	3·236	0·0308
92	34·26	—	1102	3·220	0·0295
93	34·71	—	1096	3·160	0·0285
94	35·15	—	1071	3·049	0·0280
95	35·98	1·8368	1025	3·881	0·0279
96	35·99	—	944	2·624	0·0280
97	36·38	1·8390	800	2·199	0·0286
99·4	37·20	1·8354	85	0·228	0·0400

When sulphur trioxide is added to sulphuric acid there is first an increase in the conductivity which attains a maximum and then falls rapidly to zero—the value for sulphur trioxide. The three maxima occur between water and $H_2SO_4.H_2O$, between $H_2SO_4.H_2O$ and H_2SO_4, and between H_2SO_4 and $H_2SO_4.SO_3$; and the two minima at $H_2SO_4.H_2O$ and H_2SO_4. J. L. R. Morgan and C. E. Davis found that when F. Kohlrausch's data are plotted, Fig. 96, with deviations from the mixture rule, singularities appear in agreement with the hydrates $3H_2SO_4.H_2O$, and $H_2SO_4.12H_2O$.

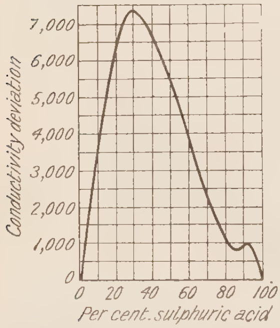

FIG. 96.—Electrical Conductivity Deviations of Sulphuric Acid from the Mixture Rule.

E. H. Loomis found the conductivity of a normal soln. of the acid at 18° to be 183×10^{-1} when referred to mercury at 4°. R. Knietsch observed that with sulphuric acid containing p per cent. of free SO_3, the resistance, R ohms, exhibits a minimum with between 14·0 and 16·7 per cent. of free SO_3, at 25°:

p .	0·34	9·8	14·0	16·7	29·5	45·0	60·3	75·0	90·0
R .	6·15	2·20	2·15	2·15	4·05	23·4	22·0	1265	61850 (36°)

E. Bouty found for dil. soln. a maximum with $H_2SO_4.500H_2O$; and with conc. soln. a minima for $2H_2SO_4.H_2O$, and $H_2SO_4.15H_2O$, and maxima for $H_2SO_4.H_2O$. H. Crompton represented F. Kohlrausch's results for the electrical conductivity, K, of $H_2SO_4.nH_2O$, by $K=-34396-758{\cdot}97p-3{\cdot}878p^2-0{\cdot}00205p^3$ when n ranges from $\frac{1}{12}$th to unity; by $K=-860+617{\cdot}5p-13{\cdot}88p^2+0{\cdot}0807p^3$ for $n=1$ to $n=2$; by $K=5321+252{\cdot}9p-7{\cdot}38p^2+0{\cdot}044p^3$ for $n=2$ to $n=6$; by $K=-1456+624{\cdot}58p-14{\cdot}191p^2+0{\cdot}0866p^3$ for $n=6$ to $n=24$; and by $K=69{\cdot}3+386{\cdot}22p-1{\cdot}494p^2-0{\cdot}1418p^3$ for $n=24$ to $n=150$. For the breaks in the curve for the second differential coefficient, d^2K/dp^2, corresponding with $H_2SO_4.SO_3$, $2H_2SO_4.SO_3$, H_2SO_4, $H_2SO_4.H_2O$, $H_2SO_4.6H_2O$, $H_2SO_4.2H_2O$, and $H_2SO_4.150H_2O$. W. C. D. Whetham gave for the conductivity, K, of very dil. soln. with M mol of H_2SO_4 per litre at 18°:

M . .	0	$0{\cdot}0_42877$	$0{\cdot}0_46100$	$0{\cdot}0_31416$	$0{\cdot}0_32835$	$0{\cdot}0_36144$
K . .	$0{\cdot}0_51005$	$0{\cdot}0_41075$	$0{\cdot}0_42324$	$0{\cdot}0_45445$	$0{\cdot}0_31077$	$0{\cdot}0_32277$

The eq. conductivity at infinite dilution was found by F. Kohlrausch to be 370 at 0°. Observations on the electrical conductivity were also made by S. Arrhenius, R. Lenz, O. Grotrian, A. Paalzoff, C. Marie and W. A. Noyes, E. Becker, A. Eucken, J. R. Pound, M. Randall and G. N. Scott, G. Tammann, F. Kohlrausch and W. A. Nippolt, H. C. Jones and co-workers, A. A. Noyes and co-workers, H. G. Klaassen, S. U. Pickering, W. Ostwald, K. Winkelblech, G. A. Hulett and L. E. Allen, F. L. Hunt, etc. D. M. Lichty gave 0·01041 mho for the conductivity of absolute sulphuric acid at 25°. R. T. Lattey studied the resistance and capacity of a pair of platinum electrodes immersed in a soln. of sulphuric acid of maximum conductivity for alternating currents of periodicity varying from 25 to 500. F. C. R. Bergius measured the conductivity of soln. of many salts in absolute sulphuric acid. The electrical conductivity of soln. of various sulphates was measured by A. F. Berggren, J. H. Long, etc. J. H. Long also discussed the relation between the electrical conductivity, the heat of soln., the velocity of diffusion, and the mol. vol. of sulphate soln.

F. Kohlrausch's observations on the effect of *temperature* on the electrical conductivity are indicated by the values for the temp. coeff. $(dk/d\theta)/K$ in the last column of Table XVI. For a normal soln., F. Kohlrausch and co-workers obtained a regular increase in the conductivity as the temp. rose from 0° to 36°:

	0°	5°	10°	15°	20°	25°	30°	35°	36°
K .	0·5184	0·5792	0·6408	0·7028	0·7645	0·8257	0·8860	0·9453	0·9570

C. Déguisne, O. Bock, S. U. Pickering, H. Rieckhoff and H. Zahn, and F. Exner and G. Goldschmidt also made observations on this subject. A. A. Noyes and co-workers obtained the following results for the effect of temp. on the eq. electrical conductivity of soln. of sulphuric acid containing C milliequivalents per litre:

C	18°	25°	50°	75°	100°	128°	156°	218°	306°
0·0 .	383	(429)	(591)	(746)	891	(1041)	1176	1505	(2030)
0·2 .	374·9	418·5	566·9	693·6	779·6	807	759	—	—
0·5 .	371·8	413·7	553·4	657·0	706·3	696	644	586	—
2·0 .	353·9	390·8	501·3	560·8	571·0	551	536	563	637
10·0 .	(309)	(337)	(406)	(435)	(446)	(460)	(481)	533	—
12·5 .	301·3	327·5	393·1	421·9	434·9	452	475	529	—
50·0 .	253·5	273·0	323·4	356·0	384·3	417	448	(502)	—
80·0 .	(240)	(258)	(306)	(342)	(373)	(408)	(440)	(488)	474
100·0 .	233·3	251·2	300·3	336·4	368·8	404	435	(483)	—

The results are plotted in Fig. 97. B. C. Felipe found that the conductivity-temp. curve of soln. of sulphuric acid is convex towards the temp. axis at high conc. and concave at low conc. With increasing dilution, the point of inflection is displaced more and more towards the lower temp. The existence of these points is explained by the antagonistic influence of the temp. on the mobility and on the degree of ionization. If the conductivity at each temp. be expressed as a function of the conc., the conductivity maxima appear most sharply defined at high temp. Occasionally two maxima are observed. K. Rogoysky and G. Tammann measured the effect of *pressure*, p atm., on the conductivity of sulphuric acid and found the resistance, R ohms, to be :

		1	101	200	300	400	498 atm.
p		1	101	200	300	400	498 atm.
R	3·941 per cent. H_2SO_4 .	(112·00)	108·70	105·80	103·22	100·81	98·582
	7·688 per cent. H_2SO_4 .	(60·12)	58·723	57·470	56·251	55·059	54·077

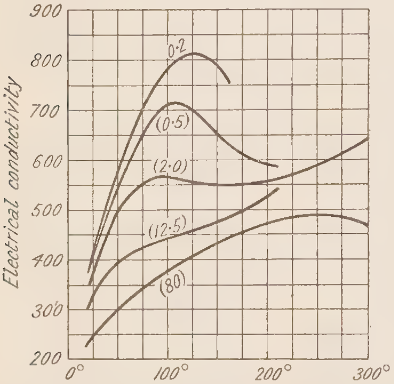

Fig. 97.—The Effect of Temperature on the Electrical Conductivity of Sulphuric Acid.

The subject was studied by G. Tammann and A. Rohmann. A. de Hemptinne found that exposure to *X-rays* had no influence on the electrical conductivity of sulphuric acid. P. Walden observed that electrolytes dissolved in sulphuric acid conduct better than in aq. soln. J. R. Pound studied the conductivity of mixtures of ether and sulphuric acid. W. C. D. Whetham measured the effect of *impurities* on the electrical conductivity of sulphuric acid, and found that with dil. soln. the conductivity is not affected by addition of a trace of potassium chloride or by boiling under diminished press., but that it is appreciably diminished in presence of a little carbon dioxide, and in this case the maximum conductivity is reached at a higher concentration. The abnormally low conductivity of dil. soln. cannot, however, be wholly attributed to the presence of carbon dioxide in the water used as solvent. S. Arrhenius found that the presence of non-electrolytes — like alcohols and sugars—reduces the ionization ; H. C. Jones, and G. Murray showed that sulphuric acid is more strongly ionized by hydrogen dioxide than it is by water. I. Kablukoff found that a mol of H_2SO_4 in v litres of alcohol at 25° had the mol. conductivities, μ :

	$v=4$				$v=8$			
Alcohol .	10	20	50	80	10	30	50	80 per cent.
μ . .	59·64	61·51	47·66	53·80	59·23	62·43	46·61	57·28

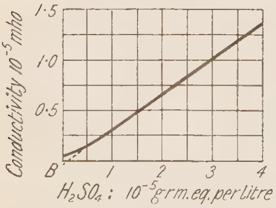

Fig. 98.—Conductivity of Dilute Sulphuric Acid.

The eq. conductivity of soln. of a neutral salt in water approaches a limiting value as dilution is increased, and this value corresponds with complete **ionization ;** with soln. of acids and alkalies, the eq. conductivity, with increasing dilution, reaches a maximum at a conc. of 0·001–0·002 grm. eq. per litre, and then falls rapidly with increasing dilution. The final drop in the eq. conductivity at extreme dilutions has been attributed to the interaction between the solute and the residual impurities in water. W. C. D. Whetham and H. H. Paine showed that carbonic acid alone will not account for the phenomenon. H. H. Paine and G. T. R. Evans believe the impurity is ammonium carbonate. If the water contains an impurity leading to an association of ions, then, if a little strong acid be added, some acid is used up and removed from activity so that the conductivity of the new soln. will be less than the sum of the constituents taken separately. This will continue until all the impurity is neutralized, and subsequent additions of acid will behave normally. Plotting the simple conductivity of the dil. acid after subtracting that of the solvent, against the conc., a straight line will be obtained for the region of normal behaviour if the acid be completely ionized. If this straight line be produced, it will cut the conductivity axis below the origin at a point B, Fig. 98, corresponding with the loss of conductivity involved in the association of the ions as above described. This agrees with the observations of H. H. Paine and G. T. R. Evans for very dil. soln. illustrated in Fig. 98, where the loss is nearly $0{\cdot}8\times10^{-6}$ mho. F. Kohlrausch found $2{\cdot}7\times10^{-6}$ mho. This loss could never be made to disappear by working with pure soln. because of the ionization of water itself, and of the recombination of the $H^{\cdot}$- and OH'-ions on the addition of the acid.

F. Bergius, A. Hollard, M. Wien, and J. Kendall and co-workers studied the conductivity of mixtures of sulphuric acid and various sulphates; K. Fredenhagen, mixtures of sulphates and in hydrofluoric acid; L. Mazza and E. Piccini, mixtures of sulphuric and nitric acids; H. K. Richardson and F. D. Taylor found that the addition of copper sulphate increases the conductivity of sulphuric acid with less than 3 grms. H_2SO_4 per 100 c.c.; if more be present, the conductivity is decreased. A. L. Ferguson and W. G. France found that the presence of gelatin reduces the conductivity of the acid. R. Kremann and W. Brassert measured the conductivity of alcoholic soln. of sulphuric acid; H. Brintzwinger studied the effects of hydrophilic colloids—*e.g.* gelatin, gum arabic, salep, and dextrin—on the conductivity and $H^{\cdot}$-ion conc. of $0{\cdot}01N$- and $0{\cdot}005N$-H_2SO_4.

J. E. Trevor [23] studied the ionization of sulphuric acid, and H. C. Jones and co-workers calculated the **degree of ionization,** α, from the mol. conductivity, μ, of soln. containing M mols of H_2SO_4 in v litres, at 0°, and from the sp. gr., and mol. lowering of the f.p., he calculated values H which were taken to represent the number of mols of water in combination with the acid at the concentration in question, when $\mu_\infty=500$:

v .	100	40	20	10	4	1·334	1·0	0·6667	0·5
μ .	398·34	353·41	335·56	314·42	296·30	281·53	259·05	234·38	209·28
α .	0·8206	0·7280	0·6913	0·6478	0·6104	0·5588	0·5337	0·4828	0·4311
H .	—	—	—	—	—	2·00	5·00	7·50	9·40

A. A. Noyes calculated values from the conductivity results indicated above and obtained for the percentage ionization, 100α, of aq. soln. of sulphuric acid containing C milliequivalents per litre:

C . .	18°	25°	50°	75°	100°	128°	156°	218°
0·2 .	98	98	96	93	87	78	65	—
10·0 .	81	79	69	58	50	44	41	35
50·0 .	66	64	55	48	43	40	38	33
100 .	61	59	51	45	41	39	37	32

where these numbers may be regarded as the minimum values of a range extending 6 to 10 units larger. G. N. Lewis and co-workers, and Y. Kato made observations on this subject. Sulphuric acid in aq. soln. is less ionized than the corresponding potassium salt, and it is resolved into three ions: $H_2SO_4\rightleftharpoons2H^{\cdot}+SO_4''$, probably passing through the intermediate stage $H_2SO_4\rightleftharpoons H^{\cdot}+HSO_4'$. W. Starck said that at high concentrations the chief ions are $H^{\cdot}$ and HSO_4', and at low concentrations $H^{\cdot}$ and SO_4''. The proportion of H_2SO_4 mols. which ionize into $H^{\cdot}$ and HSO_4'-ions probably falls with rising temp. J. A. Muller inferred that in dil. soln. the ions are $H^{\cdot}$ and HSO_4', and that these are produced with the evolution of heat; with soln. containing a mol of acid and of potassium sulphate the ions are $2H^{\cdot}$ and SO_4'' and $2K^{\cdot}$ and SO_4'' respectively. A. A. Noyes computed that in $0{\cdot}05M$-H_2SO_4, at 18°, there are 6 per cent. of H_2SO_4 mols., 61 per cent. of HSO_4'-ions, 33 per cent. of SO_4''-ions, and 127 per cent. of $H^{\cdot}$-ions. A. A. Noyes and M. A. Stewart calculated from the following percentage values from conductivity and f.p. data for soln. with M mols of H_2SO_4 per litre. The last set refers to isohydric soln.

		0°				25°			
	M-acid	$H^{\cdot}$	H_2SO_4	HSO_4'	SO_4''	$H^{\cdot}$	H_2SO_4	HSO_4'	SO_4''
Conductivity .	0·050	138	6	50	44	125	6	63	31
	0·025	148	5	42	53	133	5	57	38
	0·005	167	2	29	69	162	2	34	64
Freezing point .	0·050	122	6	66	28	117	6	71	23
	0·025	132	5	58	37	125	5	65	30
	0·005	159	2	37	61	165	2	31	67

R. C. Tolman and L. H. Greathouse found the $H^{\cdot}$-ion conc. of sulphuric acid to be 108–111, 59·7–62·0, and 31·5–35·6 per cent. respectively for $2N$-, $0{\cdot}1N$-, and $0{\cdot}05N$-soln. K. Drucker, and E. Allemann studied this subject. A. A. Noyes and M. A. Stewart calculated that a $0{\cdot}1M$-soln. of sodium hydrosulphate at 25° contains 68 per cent. of $Na^{\cdot}$-ions, 44 per cent. of $H^{\cdot}$-ions, 44 per cent. of HSO_4'-ions, 34 per cent. of SO_4''-ions, 8 per cent. of $NaHSO_4$ mols., 12 per cent. of Na_2SO_4 mols., and 2 per cent. of H_2SO_4 mols. J. Holmes and P. J. Sageman inferred, from the contractions which occur on mixing soln. of various sulphates and sulphuric acid that the mols. of hydrosulphates in aq. soln. have no individual existence, and this is in agreement with A. Colson's, and M. Berthelot's observations on the thermal data of the mixtures. M. H. Fischer and M. O. Hooker found that the electrical resistance decreases with rise of temp.; for a given temp., the resistance decreases with increasing conc. of H_2SO_4 until a minimum is attained with 50 c.c. conc. sulphuric acid of sp. gr. 1·84 and 200 c.c. of water; beyond this conc., the resistance increases rapidly and a second inflection indicates the presence of an excess of sulphur trioxide. The results indicate a change from a soln. of H_2SO_4 in water to a soln. of water in H_2SO_4.

The **ionization constant** was found by I. Traube to be 2·08 for a normal soln. R. Kremann and W. Brassert measured the degree of ionization of alcoholic soln. of sulphuric acid with M-H_2SO_4, the addition of water first diminishes and then increases the degree of ionization. Abnormal values with soln. containing a small proportion of water are attributed to the formation of the hydrate $H_2SO_4.H_2O$. Ionization increases with rise of temp. except with very dil. soln. and of soln. containing much water it diminishes with rise of temp. The effect is small, and may be due to experimental errors. K. Jellinek calculated for the first ionization constant, K_1, for $H_2SO_4 \rightleftharpoons H^{\cdot}+HSO_4'$, or $K_1[H_2SO_4]=[HSO_4'][H^{\cdot}]$, $K_1=4\times10^{-1}$ at 25° for soln. with a mol of H_2SO_4 in 2·5 to 747 litres; and K. Drucker, $K_1=2\times10^{-1}$ at 18° for soln. with a mol in 25 litres. M. S. Sherrill and A. A. Noyes gave 0·0115 for the first ionization constant in terms of the activities at 25°. K. Jellinek calculated the second ionization constant, K_2, for $HSO_4'=H^{\cdot}+SO_4''$, or $K_2[HSO_4']=[SO_4][H^{\cdot}]$, $K_2=1{\cdot}7+10^{-2}$, at 25° for soln. with a mol in 2·5 to 747 litres; R. Luther gave $K_2=0{\cdot}013$; K. Drucker, $K_2=2\times10^{-2}$, at 18°, for soln. with a mol in 25 litres; J. E. Enklaar, $1{\cdot}3\times10^{-2}$ at 18° for N-soln.; A. A. Noyes, $K_2=1{\cdot}9\times10^{-2}$, at 18°; and A. A. Noyes and M. A. Stewart, $K_2=3\times10^{-2}$, at 25°, for soln. with a mol in 10 to 40 litres. I. M. Kolthoff determined the $H^{\cdot}$-ion concentration by electrometric titration using methyl-orange as indicator, and obtained $K_2=2{\cdot}8\times10^{-2}$, and when using tropæolin OO, $3{\cdot}2\times10^{-2}$. E. Petersen calculated the **heat of ionization** to be 2·3 Cals. at about 20° for soln. with a mol of H_2SO_4 in 3·6 litres; and for the second stage of the ionization, P. T. Muller and E. Bauer gave 5·02 Cals. at 18°–20°; J. A. Muller gave 1·44 cals. at 14°, 4·21 cals. at 26°, and 3·9 cals. at 36°; and A. A. Noyes, $3575+65\theta$ cals. between 18° and 158°. W. Ostwald calculated for the heat of formation of the SO_4''-ion from its elements, 107·2 Cals. M. Randall and O. E. Cushman gave for the free energy, F, cals. of the reaction $2H^{\cdot}+SO_4''=H_2SO_4$ at 25°, for soln. of normality N:

N .	$0{\cdot}0_49009$	0·008999	0·01	0·04	0·065	0·08	0·10	0·20
F .	−9382	−6547	−3702	−1455	−85	702	1645	5272

Observations on the **electrolytic migration** of sulphuric acid were made by M. Faraday, J. F. Daniell, G. Wiedemann, W. Hittorf, E. Bourgoin, O. J. Lodge, and A. Schrader; and A. A. Noyes and K. G. Falk calculated 80 for the mobility of the $\frac{1}{2}SO_4$-ions at 25°, and infinite dilution; and F. Kohlrausch, 68 at 18°. The latter also gave for aq. soln. with *M* mols per litre, at 18°:

M . . .	0·0001	0·0005	0·001	0·005	0·01	0·05	0·1
Ionic mobility	66·6	65	63·8	58·7	55·5	45	40

W. C. D. Whetham found that the specific velocity of the SO_4''-ions is 0·00045 cm. per sec. R. Luther said that the mobility of the HSO_4'-ions is nearly the same as half that of the SO_4''-ions, being 31·25 at 15°, 38·5 at 18°, and 39 at 25°; K. Drucker gave 39 at 25°. Observations on the **transport numbers** were made by M. Huybrechts, who found 0·176 at 18° for 0·06 to 0·005*M*-soln.; O. F. Tower, who gave 0·1805 for 0·1*M*-soln. at 20° and 0·1809 for 0·01*M*-soln. at 20°; A. Eisenstein gave 0·168 for 0·124*M*-soln. at 18°, and 0·188 for 0·01*M*-soln. at 30°; W. C. D. Whetham and H. H. Paine, 0·184 for 0·05*M*-soln. at 18°; and A. L. Ferguson and W. G. France, 0·1868 for 0·1 to 0·01*M*-soln. at 25°; D. McIntosh, who found 0·174 at 18° for 1·0 to 0·001*M*-soln. Observations were also made by W. Knothe, and A. Kendrick. For soln. with *N*-gram-equivalents per litre at 19°, W. Starck gave:

N . . .	0·06	0·12	0·5	1·1	3·3	7·6
Transport No.	0·135	0·145	0·163	0·175	0·195	0·215

W. Bein found for the transport numbers of soln. with 0·05 gram-equivalents of H_2SO_4 at 11°, 33°, and 96°, respectively 0·175, 0·200, and 0·304. W. Nernst calculated for the ionization pressure of the SO_4''-anion, in normal 1·9 volts, and for the HSO'_4-anion, 2·6 volts. A. L. Ferguson and W. G. France found that the addition of 20 per cent. of gelatin increased the transport number of the sulphate ion from 0·187 to 0·685 to 0·1 to 0·01*M*-H_2SO_4. V. H. Veley and J. J. Manley concluded from their observations on the indices of refraction, and J. Domke and W. Bein from their observations on the densities, that *the substance represented by the formula H_2SO_4 is an ideal compound for it is really a mixture of molecules of H_2SO_4, SO_3, and H_2O, and it may also contain $H_2S_2O_7$.* H. S. Harned and R. D. Sturgis calculated the activity coeff. of sulphuric acid from the e.m.f. of cells $H_2 \mid M_2SO_4,H_2SO_4 \mid HgSO_4 \mid Hg$, where M_2=Mg, K_2, or Na_2—*vide infra.*

J. E. Enklaar[24] measured the **electrometric titration** curve of sulphuric acid, when 10 c.c. *N*-H_2SO_4 is diluted to 100 c.c., and titrated with 0·1*N*-NaOH at 18°. The $H^{\cdot}$-ion concentrations, expressed as p_H, are plotted as ordinates. There is no sign that the acid is dibasic, and this recalls H. E. Armstrong and F. P. Worley's hypothesis that the acid is monobasic. J. E. Enklaar interprets the result to mean that the ionization is ternary in accord with $H_2SO_4 \rightleftharpoons 2H^{\cdot} + SO_4''$. Neutralization is taken to occur when $p_H = 1{\cdot}6626$, or the $H^{\cdot}$-ion concentration is $2{\cdot}175 \times 10^{-2}$. R. Dubrisay studied the progressive neutralization of sulphuric acid with sodium hydroxide and found points of inflexion corresponding with sodium hydrosulphate, and normal sodium sulphate. F. Glaser found that by titrating 10 c.c. of 0·1*N*-H_2SO_4 with 0·1*N*-NaOH, methyl and ethyl orange as indicators showed neutralization occurred when 9·9 c.c. of alkali had been added; congo red, cochineal, lacmoid, litmus, fluorescein, and phenolacetolin with 10 c.c.; gallein, with 10·05 c.c.; rosolic acid and tropæolin OOO, 10·07 c.c.; and with alizarin, curcuma, phenolphthalein, α-naphthol-benzoin, with 10·10 c.c. Again, with 0·01*N*-H_2SO_4, and methyl orange as indicator, 9·55 c.c. of 0·01*N*-NaOH alkali were needed; congo red, 9·75 c.c.; lacmoid, 9·90 c.c.; litmus, 10·30 c.c.; and phenolphthalein, 10·70 c.c. I. M. Kolthoff worked with methyl-orange and tropæolin as indicators. As emphasized by F. W. Küster and M. Grüters, this

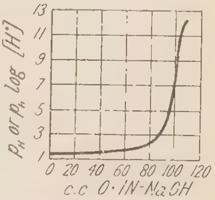

Fig. 99.—Electrometric Titration Curve of Sulphuric Acid.

shows that soln. standardized with one indicator are liable to err if used with another indicator.

The **relative affinity** of sulphuric acid was calculated by W. Ostwald on the assumption that that of hydrochloric acid is 100, and he obtained 73·9 at 25° from the velocity constant of the hydrolysis of methyl acetate; 73·2, from the velocity constant of the inversion of sugar—J. E. Trevor, and I. Spohr also studied this reaction; 59·4, from the velocity constant of the hydrolysis of acetamide; 65·1, 65·4, and 59·4 from the electrical conductivities of the acid respectively at 25°, 65°, and 100°; and 66 from the partition of the two acids with alkali; while R. Hoepke gave 57·9 from the effect of the acids on the reaction between iodic and sulphurous acids; and I. Kablukoff, 59·23–59·64 from the electrical conductivities of the acids in alcoholic soln. W. Ostwald examined the effects of the acids on other reactions. H. Colin and A. Chaudun discussed the hydrolysis of sucrose by the dil. acid. H. Frey found that the presence of neutral salts diminishes the activity of the acid. S. A. Kay made estimates of the free acid in a mixed soln. of sulphuric acid and normal alkali sulphate from the effect on the hydrolysis of ethyl acetate. J. Thomsen, and W. Ostwald also calculated values from the distribution of a base between two acids. The relative affinities of a few acids can be represented by

Acid.	Sugar inversion.	Hydrolysis methyl acetate.	Hydrolysis acetamide.	Division of base.	Electrical conductivity.	Catalysis HIO_3+SO_2.
Hydrochloric	100	100	100	98	100	100
Hydrobromic	105·5	99·1	98	89	101·1	—
Hydriodic	—	98·1	—	—	—	—
Nitric	100	95·7	98	100	99·6	83
Chloric	101·8	97·2	—	—	—	—
Sulphuric	73·2	73·73	65·4	66	65·1	58
Phosphoric	24·9	—	—	25	7·27	9
Arsenic	21·9	—	—	—	5·38	—

H. S. Harned and R. D. Sturgis, M. Randall and C. T. Langford, M. Randall and G. N. Scott, G. N. Lewis and M. Randall, and G. Akerlöf measured the activity coefficients of sulphuric acid as the sulphates.

W. Henry,[25] W. Cruickshank, P. L. Simon, and W. Hisinger and J. J. Berzelius observed that in the **electrolysis** of conc. sulphuric acid, with a platinum anode only a little hydrogen is evolved, the greatest part is consumed by secondary reactions in the reduction of the acid to sulphur and a little hydrogen sulphide. M. Faraday observed that in the electrolysis of conc. sulphuric acid, oxygen is evolved at the anode, and sulphur and hydrogen are formed at the positive pole; and he was impressed with the fact that "if the acid be very strong, a remarkable disappearance of oxygen took place." C. Luckow, however, showed that the results are different with the dil. acid, or with the acid formed during the electrolysis of aq. soln. of the sulphates. R. Weber observed that with conc. sulphuric acid, some sulphur sesquioxide may be formed, and also blue colloidal sulphur. E. Warburg found that in the electrolysis of sulphuric acid mixed with two-thirds its vol. of water, the theoretical amount of hydrogen is given off at temp. up to 80°, at higher temp. less hydrogen is given off and sulphur is formed. With a higher current density, a higher temp. is necessary for this change, and with a lower current density a lower temp. By diluting the acid still more, a higher temp. is necessary to produce sulphur, and with a mixture of equal vols. of water and the conc. acid, hydrogen alone appears at the cathode at all temp. A. Geuther supposed that the sulphuric acid is directly decomposed into sulphur, hydrogen, and oxygen, and with the less conc. acid, hydrogen and sulphurous acid are formed at the cathode. A. Guerout said that the sulphurous acid is broken down by the current into hyposulphurous acid. W. R. Cousins, and V. Schischkin studied the electrolytic oxidation of sulphuric acid; and A. Klemenc found that the amounts of hydrogen and oxygen obtained with *n* coulumbs were:

N-H_2SO_4	0·1	1·0	2·0	5·0	10·0	16·0
n coulombs	658	640	718	721	810	803
Total O	4·0	5·2	8·9	18·9	18·2	11·6
Hydrogen	111	115	121	145	140	124

The oxygen in the first case was obtained as gas; in the second, partly as gas and partly in the electrolyte; and in the other cases, wholly in the electrolyte—*vide infra*, the persulphuric acids. A. Mazzucchelli and B. Romani discussed the influence of perchlorate ions on the overvoltage at the anode in the electrolysis of sulphuric acid resulting in an increased yield of persulphuric acid. M. Berthelot distinguished between sulphur, insoluble in carbon disulphide formed by secondary reactions at the cathode, and that deposited on the anode by the electrolysis of hydrogen sulphide which might be present in the liquid; he called the former *electropositive sulphur*, and the latter *electronegative sulphur*. For the electrolysis of dil. sulphuric acid, *vide* **1**. 3, 6. M. Berthelot discussed the smallest e.m.f. needed to electrolyze soln. of the metal sulphates; and J. Vuillermoz, the reversible e.m.f.

J. W. Clark found that a pressure of 300 atm. is not sufficient to prevent the electrolysis of dil. sulphuric acid when a sealed-tube of sulphuric acid is electrolyzed fixed vertically so that a lower electrode is positive and an upper electrode is negative, a layer of conc. sulphuric acid forms about the lower electrode and water collects about the upper electrode. If the electrodes be reversed, the conc. sulphuric acid forms about the upper electrode, but it is then mixed with the liquid by rapid diffusion and by the agitation with the rising bubbles of gas. Nothing has been done with J. W. Clark's suggestion that this "singular action affords a means of concentrating sulphuric acid without boiling." Z. Stary studied the electro-osmosis of sulphuric acid in an electric field of high-tension. A. Coehn and R. Schnurmann studied the electric discharge in sulphuric acid.

According to J. H. Gladstone and A. Tribe, with 98·2 per cent. H_2SO_4, and a sufficient voltage, sulphur slowly forms a film over the platinum cathode. This retards the occlusion of hydrogen by the metal, and the hydrogen escapes. They observed no sign of the reduction of the sulphuric acid by the hydrogen liberated when the film of sulphur has formed on the platinum; on the other hand, if the voltage is weak enough, no hydrogen or sulphur appears at the cathode, but the liquid contains sulphur dioxide in soln. This inference was confirmed by their study of hydrogenized palladium or platinum on sulphuric acid. They also observed that the evolution of oxygen from both electrodes could be detected for several days after the circuit had been broken; and they attributed the phenomenon to the slow decomposition of M. Berthelot's *l'acide persulfurique* formed during the electrolysis of the sulphuric acid. Persulphuric acid, S_2O_7, said M. Berthelot, is formed at the anode during the electrolysis of dil. sulphuric acid, say, at a conc. $H_2SO_4 : 10H_2O$; if the conc. is $H_2SO_4 : 4H_2O$, hydrogen dioxide is formed, and this combines with *l'acide persulfurique*, forming $S_2O_7.2H_2O_2$, and a large yield of this substance is obtained when the conc. of the electrolyte is $H_2SO_4 : 2$ to $3H_2O$. With more conc. sulphuric acid, the yield is reduced. H. Marshall prepared perdisulphuric acid, $H_2S_2O_8$, by the electrolysis of alkali sulphates. M. Traube reported that in the electrolysis of sulphuric acid, say 40 per cent. H_2SO_4, the sulphur oxide which decomposes potassium iodide is not S_2O_7, but rather SO_4, because the ratio of H_2SO_4 to active oxygen is greater than 2 : 1 being nearer 1 : 1. He called this compound *sulphuryl holoxide*, because he regarded it as a mol. compound $SO_2.O_2$. M. Berthelot, and D. Carnegie showed that M. Traube's holoxide was probably a mixture of perdisulphuric acid and hydrogen dioxide, an explanation which was later accepted by M. Traube himself. According to N. Caro, M. Berthelot's original *l'acide persulfurique*, and M. Traube's sulphuryl holoxide were probably permonosulphuric acid, H_2SO_5. According to A. von Bäyer and V. Villiger, with 20 per cent. sulphuric acid, the perdisulphuric acid gradually changes into permonosulphuric acid, but on electrolyzing more conc. acids, the permonosulphuric acid is largely formed during the electrolysis. Consequently, both M. Berthelot, and

M. Traube were right, since all depends on the working conditions. F. Richarz explained the transport number, and the formation of *l'acide persulfurique* by the electrolysis of sulphuric acid of medium concentration—about 50 per cent. H_2SO_4—by assuming that HSO_4-ions are formed. K. Elbs and co-workers suggested that in very dil. soln., sulphuric acid is ionized: $H_2SO_4 \rightleftharpoons 2H^{\cdot} + SO_4''$, and that on electrolysis, the hydrogen is discharged at the cathode, while at the anode, the SO_4-ion reacts: $SO_4 + H_2O = H_2SO_4 + O$. On the other hand, sulphuric acid, of sp. gr. 1·4, is ionized: $H_2SO_4 \rightleftharpoons H^{\cdot} + HSO_4'$, and on electrolysis the hydrogen is discharged at the cathode, and the two HSO_4'-ions are doubled to form perdisulphuric acid: $2HSO_4 = H_2S_2O_8$. V. Kuriloff observed the formation of both hydrogen dioxide and *l'acide persulfurique* according to the conditions. The latter appears first when 10 per cent. of H_2SO_4 is present; and hydrogen dioxide with 3 to 47 per cent. H_2SO_4. E. Bouty said that a molecule of the type $H_2SO_4.H_2O$ should split up into hydrogen, sulphur trioxide, and hydrogen dioxide. As a matter of fact, hydrogen dioxide is a normal product of the electrolysis of acid of this strength. According to F. Richarz, the maximum amount of hydrogen dioxide is obtained when the acid has the composition $H_2SO_4 + 1{\cdot}347H_2O$. With acid below 60 per cent., very little hydrogen dioxide is formed, but persulphuric acid and ozone are produced in considerable quantities. It may be assumed that the apparent limit at $H_2SO_4 + 5H_2O$ or $6H_2O$ really corresponds with the complete disappearance of hydrogen dioxide from the products of electrolysis, or, in other words, with the complete destruction of molecules of the type H_2SO_4,H_2O, whilst the limit at $H_2SO_4 + 15H_2O$ corresponds with the complete disappearance of persulphuric acid from the products, or with the destruction of the unknown hydrate intermediate between the monohydrate and that which exists in very dil. soln.

M. Berthelot found that besides *l'acide persulfurique*, sulphuric acid of sp. gr. 1·4, when electrolyzed with a thin platinum wire sealed into a glass tube, furnished oxygen containing about 0·5 per cent. of ozone. The formation of ozone by the electrolysis of dil. sulphuric acid was observed by C. F. Schönbein, J. C. G. de Marignac, A. W. Williamson, H. Meidinger, F. M. Baumert, T. Andrews, J. Tyndall, L. Soret, B. C. Brodie, J. W. Clark, H. Hoffmann, E. Schöne, L. Carius, H. McLeod, etc.

For J. Meyer and A. Pawletta's observations on mixtures of sulphuric and phosphoric acid, *vide* phosphoric acid. H. Hoffmann electrolyzed 98·3 per cent. sulphuric acid—sp. gr. 1·841 at 18°/4°—at various temp. by currents of various strengths. He found that at 50°, independently of the current strength, hydrogen, hydrogen sulphide, and sulphur are produced on the cathode, whilst at higher temp. sulphur dioxide and sulphur are produced, and in the neighbourhood of 300° only sulphur is obtained. Oxygen is liberated from the anode at these temp. At 200°, the oxygen is mixed with sulphur dioxide, produced from sulphur which has diffused from the cathode chamber, and has been oxidized by the hot sulphuric acid and the nascent oxygen. From 280° upward, sulphur dioxide and oxygen are liberated in quantities corresponding with Faraday's law. The gas element $SO_2 | O_2$, in consequence of incomplete charging of the electrodes, does not furnish the expected e.m.f., and also the velocity of reaction of the gases is too small for the production of large quantities of current. The decomposition voltage of hot, conc. sulphuric acid lies near to that of water, that is, higher than the calculated and observed values of the potential difference of the gas element. From this it follows that the primary products of electrolysis are hydrogen and oxygen whilst sulphur dioxide is a secondary product—*vide* **1.** 14, 2.

K. Elbs showed that if the sulphuric acid has iron in soln., less electrolytic gas is produced than corresponds with Faraday's law, with acid of sp. gr. 1·175 containing one per cent. of iron, 97·4 per cent. of the theoretical yield is obtained. According to J. A. Muller, in the electrolysis of a mol. soln. of sulphuric acid in a porous pot, as cathode chamber, immersed in a vessel containing a mol. soln. of potassium hydroxide, the hydrogen liberated is in excess of the hydrogen eq.

of the potassium which has travelled to the cathode, and of the sulphate which has passed to the anode. This is attributed to the partial ionization of the potassium hydroxide to H˙- and OK′-ions. If the alkali hydroxide soln. be replaced by hydrochloric acid, an excess of hydrogen is again obtained. This is attributed to the formation of oxygenated chlorine compounds. If the alkali hydroxide be replaced by gold chloride, hydrogen is given off at the cathode, and slightly ionized oxygen at the anode. No gold is deposited. F. Richarz observed that in the electrolysis of dil. sulphuric acid, with a rising strength of current, when a potential difference of 1·08 volts is attained, there is not only a sudden rise in the strength of the current, as observed by H. von Helmholtz, but hydrogen dioxide is formed at the cathode by the reduction of dissolved neutral oxygen. F. Richarz and C. Lonnes observed that hydrogen dioxide is not produced when platinum and gold electrodes are used although they contain occluded hydrogen, but convection currents may result in the formation of hydrogen dioxide, but the quantity produced is not sufficient to account for the current, and it is in no way proportional to the current strength. F. H. Jeffery found that when sulphuric acid is electrolyzed with a gold anode a little gold passes into soln. and a complex salt is formed with gold in the anion. E. Elsässer found that hydrogen is developed at both electrodes when dil. sulphuric acid is electrolyzed with a magnesium anode and a platinum cathode; and with very dil. acid, twice as much hydrogen is given off from the platinum electrode. H. Highton said that if the acid be electrolyzed with a zinc anode and carbon cathode, hydrogen sulphide is formed at the anode, but W. Skey attributed the hydrogen sulphide to the presence of sulphides in the carbon or to hydrogen sulphide adsorbed from the atmosphere. A. Bartoli and G. Papasogli observed that in the electrolysis of sulphuric acid with a carbon anode, besides carbon monoxide and dioxide, there is formed black *mellogen*, $(C_{14}H_2O_4)_n$, together with traces of benzocarboxylic acids produced by the oxidation of mellogen; with a graphite electrode, graphitic acid, $(C_{14}H_2O_4)_n$, is formed. F. Haber electrolyzed heated sulphuric acid in vacuo, with the cathode suspended a few mm. above the liquid, using a voltage of 600, and found more hydrogen is produced than corresponds with Faraday's law—permonosulphuric and perdisulphuric acids were formed in the liquid, and more of these substances were formed when the anode was suspended above the liquid. The yield of active oxygen—hydrogen dioxide and the two persulphuric acids—increases with the conc. of the acid up to 45 per cent. H_2SO_4; it then falls off until, with 75 per cent. H_2SO_4, none is produced. If oxygen at a press. of 131 mm. is contained in the chamber, there is also a drop in the yield of active oxygen. It is inferred that at the electrode a strong oxidizing product is formed from the water; this is taken up by the liquid, and it is sufficiently stable to oxidize the sulphuric acid, forming hydrogen dioxide, and the two persulphuric acids.

J. Tafel and B. Emmert observed that when dil. sulphuric acid is electrolyzed with a platinum anode, the current density at that electrode being comparatively low, chemically recognizable quantities of platinum are dissolved. These small quantities of platinum suffice to account for the observed depressions of the cathode potential. The sensitiveness of different cathode metals varies considerably; in the case of a silver cathode, 0·00001 mg. of platinum is able to produce the depression of the potential for a cathode surface of 10 sq. cms. The effect is produced by the precipitation of the platinum on the cathode, but even then it may remain latent. The action of the platinum is apparently not to convert the cathode into a platinum cathode, but to assist catalytically some chemical change of the cathode surface. The action of gold on the cathode potential of other metals is insignificant compared with that of platinum. J. Violle and M. Chassagny observed that if a positive electrode consisting of a platinum wire 4·5 mm. in diameter is plunged to a considerable depth in water containing 10 per cent. of sulphuric acid, and a negative electrode consisting of a platinum wire 1·5 mm. in diameter is gradually immersed in the liquid, then, if the difference of potential between the two electrodes is not less than 32 volts, there is seen round the negative electrode a luminous sheath which separates it from the liquid and in which alone the evolution of hydrogen takes place. This sheath offers a very high resistance, which gradually diminishes as the length of wire immersed increases and falls very suddenly at the moment when the luminous sheath disappears and gives place to a train of bubbles of hydrogen. The length of the luminous sheath increases with the electromotive force, and the quantity of energy used up in the electrolytic cell is proportional to the length of the luminous sheath which the particular current can produce. The luminosity is not continuous, and at first it consists only of points of orange light at the extremity of the electrode, but these become violet in colour and extend over the whole of the submerged wire. The electrodes become very hot, and if the circuit is broken the luminosity does not disappear immediately, and there is a hissing sound when the water comes in contact with the hot wire. The displacement of the luminous sheath by a train of bubbles of gas, which takes place when the electrode is immersed to a certain depth, is accompanied by a kind of explosion. U. Pomilio reduced some unsaturated aliphatic acids by the electrolyses of alcoholic soln. in the presence of sulphuric acid; and he found that dil. soln. of sulphuric acid in alcohol are reduced by electrolytic hydrogen liberated from a nickel or lead cathode, sulphur and hydrogen sulphide occurring among the products of the reduction. On the other hand, ethyl alcohol acidified with hydrochloric acid is not appreciably attacked by cathodic hydrogen under widely varied conditions.

H. Jahn[26] determined the e.m.f. of the **polarization** produced with soln. of sulphuric acid, and compared it with the e.m.f. produced with different pairs of salt soln. so as to get an idea of the magnitude of the secondary heat effect as distinct from that due to electrical resistance. The e.m.f of the polarization between platinum electrodes is 2·388 volt. The total heat effect is 0·11007 Cal., and the calculated secondary heat effect is 0·04171 Cal. These numbers are in agreement with the observed heat effects. J. B. Westhaver found that anodes of iridium, platinum, and rhodium behave differently in $0{\cdot}1N\text{-}H_2SO_4$. When the current density is high, iridium is the least polarizable, followed by rhodium; at low values of the current density, platinum is less easily polarized than iridium. A considerable interval elapses before the stationary condition of affairs is reached. When the logarithm of the current is plotted against the electrode potential, curves are obtained for the various kinds of platinum and iridium electrodes, which all exhibit a break at 1·45 volts. Electrodes of iridium black, on account of their small polarization, are suitable for determinations of conductivity with alternating current and a telephone. According to E. Bouty, the e.m.f. of polarization of platinum electrodes is 1·2 to 1·3 volts with the strongest acid, but this gradually diminishes with dilution until it is only 0·7 to 0·8 volt when the composition is H_2SO_4,H_2O. It retains this value until the composition of the liquid becomes $H_2SO_4+5H_2O$ or $6H_2O$, and at this point it rises suddenly to 1·4 volts, but afterwards gradually although very slowly diminishes. The polarization effect was also studied by J. Tafel using dil. sulphuric acid, a platinum anode, and cathodes of various metals. The cathode potential, E, is related with the current density, I, by $E=a+b \log I$, where a and b are constants for a given temp. The potentials all decrease as the temp. rises, but with mercury b increases with rise of temp. The applicability of the formula may be masked by secondary changes. The primary influence of the cathode surface, so far as its mechanical properties are concerned, appears to be comparatively slight; for example, polished and prepared lead electrodes have approximately the same polarization values. But the cathode process itself effects mechanical and chemical changes at the surface of the cathode, and these changes influence the potential values so that the latter are more or less dependent on the previous history of the cathode. Some metals (lead, cadmium, silver, and copper) exhibit two distinct polarization states when the anode liquid has access to the cathode, a state of "elevation" and a state of "depression." The change from the one to the other takes place during electrolysis, and often occurs suddenly—*vide supra*. The potential at all the cathodes (those of platinized platinum and mercury excepted) changes slowly during electrolysis. When the cathode is protected from the anode liquid, lead, cadmium, tin, and bismuth all reach a polarization maximum within a short time, up to half an hour in the last two cases. With copper, nickel, gold, and bright platinum, the cathode potential for a given current density goes on increasing for hours, and with platinum no maximum value can be reached at all. J. Tafel said that the observed data are rather opposed to the view of varying polarization as due to the varying thickness of a gaseous layer on the electrode, and he regards the cathode surface as having in different cases a different catalytic effect on the process of formation of hydrogen gas. E. E. Zimmerman studied the effect of temp. on the polarization capacity of gold and platinum electrodes in sulphuric acid of different concentrations; D. Reichinstein and W. von Reyter, W. M. Pierce, L. J. P. Byrne, and I. Wolff also investigated this subject. S. Glasstone studied the anodic overvoltages of lead, iron, nickel, and platinum in N-H_2SO_4—*vide* the overvoltage of hydrogen, **1**. 7, 8. According to A. A. Noyes, the contra-electromotive force of sulphuric acid at 20° is 1·68 volts, and diminishes at first inversely as the absolute temp. Between 60° and 120°, it diminishes more rapidly, and above the latter temp. remains practically constant. This may be due to a difference in the mode of ionization which is at first into $H^+ + HSO_4^-$—and then $2H^+$ and SO_4^{--}. S. Glasstone measured the cathodic and anodic overvoltages of a number of metals in N-H_2SO_4.

G. Tammann studied the electrolysis of sulphuric acid. According to B. G. Cobb, in the electrolysis of conc. sulphuric acid with aluminium electrodes and a current of 200 volts through an external resistance of 300 ohms, the resistance is at first almost zero, but soon rises so that in half a minute only 0·021 amp. of current was passing. The resistance is due to a non-conducting film of hydrogen, forming on the metal. The evolution of gas from the anode is accompanied by vigorous sparking, which becomes more marked with increasing amperage. The liquid gradually becomes turbid owing to the separation of a basic aluminium sulphate. If a dry glass rod be caused to touch the top of the anode during electrolysis, an arc is produced under the liquid between the aluminium plate and the glass rod held in the hand. If the cathode be an aluminium plate, and the anode a stout aluminium wire wound round with glass-wool, on passing the current, an arc starts between the anode and the glass-wool beneath the surface. With copper electrodes the sparks are red; with silver or platinum there is no sparking. According to S. Marsh, in the electrolysis of sulphuric acid by an alternating current, and with electrodes of platinum foil, the amount of evolution of gas decreases rapidly with time, and eventually no more gas is evolved. The amount evolved decreases with increasing frequency of the current; when thin platinum electrodes were used, the amount was less, but no simple relationship between the volume of gas evolved and the thickness of the electrode was observed. The time-volume curves resemble the saturation curves obtained in radioactive measurements. With gold electrodes, the rate of evolution of gas falls off rapidly with time, but for frequencies less than 48, gas is still given off at the electrodes for a much longer time than with platinum, and the total vol. of gas are considerably smaller than in the case of platinum. In the case of nickel electrodes, a copious evolution of hydrogen occurred for twenty minutes, beyond which the experiment could not be continued, owing to soln. of the electrode.

F. Streintz[27] measured the **contact electromotive force** between the metals and soln. of their sulphates. S. Pagliani said that mere contact of a soln. of copper sulphate with a soln. of a sulphate of potassium, sodium, lithium, magnesium, cadmium, or zinc produces a current which flows from the sulphate soln. to the soln. of copper sulphate; and with suitable concentrations, a current passes from a soln. of sulphate of potassium, sodium, lithium, magnesium, nickel, iron, manganese, cadmium, zinc, copper, cobalt, and aluminium to the soln. of the next sulphate in the series. The constant e.m.f. of sulphate soln. with conc. sulphuric acid decreases with increasing conc. of the acid; and with dil. sulphuric acid, the e.m.f increases with increasing conc. of the sulphate soln. J. A. Crowther and R. J. Stephenson measured the contact resistance between sulphuric acid and a polarizable electrode immersed therein. H. S. Harned and R. D. Sturgis measured the **electromotive force** of cells of the type $H_2 \mid M_2SO_4,H_2SO_4 \mid Hg_2SO_4 \mid Hg$, where M represents Na or K; and $H_2 \mid MgSO_4,H_2SO_4 \mid Hg_2SO_4 \mid Hg$; and G. Akerlöf, the e.m.f. of cells $H_2 \mid H_2SO_4,M_2SO_4 \mid Hg_2SO_4$ with different concentrations of acid and of M_2SO_4 represented by lithium or sodium sulphate. D. F. Smith and J. E. Mayer studied the e.m.f. of cells of the type: $H_2(Pt) \mid H_2SO_4+HCl,H_2SO_4+HI+I_2 \mid Pt$; and also concentration cells of sulphuric acid. Referring back to the **reduction potentials** of sulphur, hydrogen sulphide, and sulphur dioxide, sulphuric acid should, from the equilibrium standpoint, be capable of reduction to sulphur and hydrogen sulphide by very mild reducing agents, the fact that this does not occur in practice is doubtless due to marked passivity or slow reactivity of the sulphate ion. Any reducing agent strong enough to reduce sulphuric acid to sulphurous acid should be capable of reducing it completely to hydrogen sulphide, thus showing that it is impossible to realize stable equilibrium conditions between these two acids at 25°. Sulphuric or sulphurous acid may, however, be reduced to sulphur, without producing hydrogen sulphide; but the formation of the latter is favoured by large $H^{\cdot}$-concentration. A. Oberbeck and J. Edler measured the e.m.f. of amalgams of zinc, cadmium, tin, lead, and bismuth against mercury in dil. sulphuric acid and in various salt soln. The metals follow this order in the magnitude of the e.m.f. G. Gore observed that the **thermoelectric force** between sulphuric acid and a mercury electrode increases with the conc. of the acid until with soln. containing one of acid to 39 of water the e.m.f. begins to increase, and with a concentration 1 : 19, it again increases. L. G. Gouy studied the relation between the height, h, of a column of mercury balanced by **electrocapillary forces** and the difference of potential, E, between the mercury and soln. of sulphuric acid of different conc. The values of h decrease with concentration; d^2h/dE^2 is always negative, so that the curve has no point of inflexion, and does not tend to any limiting value. T. Svensson, and J. Lifschitz and S. B. Hooghoudt studied the **photoelectric effect,** or change in potential of an electrode in sulphuric acid when illuminated—the *Becquerel effect.*

According to J. Blake, no **convection of electricity** occurs during the evaporation of the charged acid. R. Sabine observed that when drops of dil. sulphuric acid are placed on the clean surface of amalgams of lead, tin, antimony, zinc, or copper, the drops are seen to move about with a more or less jerky motion, the area of the drops undergoing successive irregular contractions and expansions. He explains the phenomenon as being due to alternate oxidation by the air outside the drop, and deoxidation by electrolysis in the interior of the drop, of a portion of the surface of the amalgam. When the metal amalgamated with mercury is specifically lighter than that metal, the surface of the amalgam consists of mercury in which float innumerable particles of the foreign metal. When the drop of acid comes into contact with such a surface, currents are generated, through the acid, between the mercury and foreign metal. If the foreign metal be positive to mercury, the latter is deoxidized underneath the drop and therefore cleaned: the adhesion between the drop and this clean surface is less than that between the drop and the original surface, the drop therefore contracts, and in so doing exposes a clean surface of mercury to the air; this again becomes superficially oxidized, whereupon the original state of matters is restored. S. Wosnessensky measured the potential difference at the surface of contact of sulphuric acid with a non-aq. solvent with normal calomel electrodes.

P. Walden[28] said that the **dielectric constant** of conc. sulphuric acid is over 84 for $\lambda=73\times10^4$ cm. With mixtures of sulphuric acid and water, R. Weber observed no relation between the conductivity and the dielectric constant, which ranges from 39 to 47·9. J. Dewar and J. A. Fleming found that the dielectric constant is a function of the frequency and temp., lowering the temp., and reducing frequency reduce the dielectric constant. G. Akerlöf studied the dielectric constants of sulphuric acid in the formula for the relation between the dielectric constants of a medium and the solubility of electrolytes. J. Königsberger [29] gave $-2\cdot76\times10^{-6}$ for the **magnetic susceptibility** at 22°; and G. Quincke, $-0\cdot80\times10^{-6}$ at 19°. G. Jäger and S. Meyer studied the magnetization of soln. of the sulphates of manganese iron, cobalt, and nickel.

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§ 31. The Chemical Properties of Sulphuric Acid

According to W. Vaubel,[1] a number of the reactions of sulphuric acid depend on the hydrates which are present in the soln., rather than on the degree of electrolytic ionization. Amongst these are the green coloration with phenylrosinduline at conc. below 95·2 per cent., the formation of hydrogen sulphide from sodium thiosulphate at conc. above 84·1 per cent., and the series of colours produced at different conc. in safranine solutions. Estimates of the *affinity* of sulphuric acid have been previously considered. J. Fiedler said that sulphuric acid is decomposed, giving off oxygen when exposed to light, but this lacks confirmation.

A. Christoff measured the solubility of **hydrogen** (*q.v.*) in sulphuric acid ; and J. A. Wanklyn and W. J. Cooper, in mixtures of nitric and sulphuric acids. According to A. F. de Fourcroy, when the vapour of sulphuric acid mixed with hydrogen is passed through a red-hot tube, water and sulphurous or sulphuric acid or hydrogen sulphide are formed according to the proportion of hydrogen present ; A. Vila also observed that when sulphuric acid vapour mixed with hydrogen is passed over silica heated to 700°–900°, quantitative reduction to hydrogen sulphide occurs. According to S. Cooke, conc. sulphuric acid is not reduced by hydrogen at ordinary temp., but if finely divided platinum be present, the hydrogen slowly contracts, and sulphur dioxide is formed. J. Milbauer said that sulphur dioxide is formed when impure hydrogen is bubbled through sulphuric acid, but not so with purified hydrogen. F. Jones, however, said that if hydrogen be left in contact with sulphuric acid for a few days at ordinary temp., the vol. of gas gradually contracts owing to the reduction of the sulphuric acid to sulphur dioxide. C. J. Warner found that the reduction of sulphuric acid by hydrogen begins at 160°, and sulphur dioxide is formed. R. H. Adie gave 170°, and observed no sign of hydrogen sulphide. According to M. Berthelot, a slow current of hydrogen can be passed for an hour through conc. sulphuric acid at the ordinary temp. without any appreciable production of sulphur dioxide, but if contact between the gas and the acid is prolonged, the gas is absorbed and the acid is reduced. Light has no distinct influence on the reaction. Dil. sulphuric acid is not reduced by the hydrogen. At 250°, with the conc. acid, reduction takes place somewhat rapidly, especially in presence of a considerable excess of acid. When mixtures of hydrogen and oxygen are left in contact with sulphuric acid either at the ordinary temp. or at 250°, both gases are absorbed, but the rate of absorption of hydrogen is the same as in the absence of oxygen, and the absorption of oxygen is due to its combination with the sulphur dioxide that is formed. Dry hydrogen and sulphur dioxide do not interact at 100° or 280°. The reduction of conc. sulphuric acid by hydrogen is an exothermic reaction and develops 15·1 Cals, this value being increased to 30·1 Cals. in the presence of a large excess of sulphuric acid, owing to the heat of hydration. In the case of dil. sulphuric acid, the reaction would be endothermic. J. Milbauer found that the rate of reduction of sulphuric acid, with between 91 and 97 per cent. H_2SO_4, is constant when the gas is bubbled through the acid at 174°. The reaction between hydrogen and sulphuric acid is increased by the presence of various catalytic agents—notably by metals of the platinum group, but also by gold, and selenium, the soluble sulphates of copper, mercury, cerium, and lanthanum, and the oxides of arsenic, antimony, and tantalum. The presence of the oxides of vanadium, molybdenum, and tungsten, or other suspended substances like silica, diminishes the yield of sulphur dioxide, and the same result is obtained to a very slight extent with the alkali and alkaline earth sulphates. The catalytic effect increases with the concentration up to a limiting value which corresponds with the limit of the solubility of the sulphate; with mercuric sulphate there is an appreciable action at 26°, and the action increases rapidly with rise of temp. Some substances—*e.g.* ferrous and mercurous sulphates, and tellurium—are oxidized in spite of the presence of hydrogen and sulphur dioxide; selenium shows an alternate sequence of oxidations and reductions; while osmium tetroxide, palladium and cerium sulphates, selenium dioxide, and the oxides of vanadium, molybdenum, and titanium are first reduced. Light has no appreciable influence on the reaction. J. Milbauer found that the maximum catalytic effect is obtained when the sulphuric acid is saturated, but not supersaturated, with soluble platinum sulphate. This occurs most readily if the sulphuric acid be treated with platinum black. Arsenic trioxide retards the reaction. As indicated in connection with sulphur, hydrogen sulphide, and sulphur dioxide, these substances may be produced by the action of hydrogen *in statu nascendi* on sulphuric acid. M. Faraday observed that sulphur and hydrogen appear at the cathode in the electrolysis of sulphuric acid (*q.v.*). J. H. Gladstone and A. Tribe found that hydrogen occluded in platinum reduces sulphuric acid to sulphur dioxide and sulphur.

O. F. Tower[2] measured the solubility of **air** (*q.v.*) in sulphuric acid, and A. Christoff, and C. Bohr, that of **oxygen** (*q.v.*). The subject was studied by G. Tammann. Sulphuric acid has no chemical action on oxygen; according to C. D. Harries, moderately dry **ozone** is not affected by being passed through conc. sulphuric acid, whereas, under the same circumstances, ozone which has been dried over phosphorus pentoxide is decomposed to the extent of one per cent. by the acid. Sulphuric acid can be mixed with **water** in all proportions; and when the acid is exposed to an atm. sat. with moisture, J. L. Gay Lussac said that it can absorb fifteen times its weight of water; and H. W. Hake found that the maximum **deliquescence** on exposure to air was to convert 95·8 per cent. H_2SO_4 into 35·37 per cent. H_2SO_4.

The vap. press. of sulphuric acid of different concentrations has been previously discussed; obviously, in any closed space, the concentration of the acid determines the humidity of the atmosphere. The distribution of the moisture between sulphuric acid and the atm. has been discussed by W. I. Busnikoff—*vide supra,* the desiccating power of sulphuric acid. The great affinity of sulphuric acid for water is evidenced by its hygroscopicity and its use in desiccators, and in the balance case for keeping a dry atmosphere in these vessels; and also for drying gases. Sulphuric acid acts upon many solid and liquid substances depriving them of water; or even decomposing the substance—splitting off the elements of water when no ready-formed water is present. Wood, paper, sugar, starch, and many organic substances are blackened by conc. sulphuric acid owing to the separation of carbon which accompanies the removal of the elements of water. This property is utilized for the preparation of carbon monoxide; for the preparation of ethylene. The effect is easily demonstrated by stirring 10 grms. of powdered cane sugar with 12 grms. of conc. sulphuric acid in a beaker. The sugar first becomes pale brown, rapidly darkens in tint, and finally becomes black; at the same time, much steam is evolved and the mass swells up considerably. According to A. von Bäyer and V. Villiger, **hydrogen dioxide** reacts with conc. sulphuric acid, forming permonosulphuric acid, H_2SO_5; and T. M. Lowry and J. N. West studied the equilibrium conditions in the reactions $H_2O_2+H_2SO_4 \rightleftharpoons H_2SO_5+H_2O$, and $H_2O_2+2H_2SO_4 = H_2S_2O_8+2H_2O$—*vide infra;* and R. Glocker and O. Risse, the photochemistry of the reaction. M. Berthelot added:

> L'acide persulfurique se forme également, toujours à l'état dissous, lorsqu'on mélange avec précaution et en évitante toute élévation de température une solution d'eau oxygénée avec l'acide sulfurique soit concentré, soit étendu d'une quantité d'eau inférieure à l'équivalent. Mais la combinaison n'a point lieu quand l'acide sulfurique est étendu à l'avance de 2 équivalents d'eau, ou davantage. Dans tous les cas, elle demeure partielle, c'est-à-dire qu'il subsiste une portion de l'eau oxygénée.

H. Moissan[3] found that sulphuric acid is partly decomposed by **fluorine;** and F. Fichter and K. Humpert, and W. Bladergroen found that persulphuric acid is formed (*q.v.*). Sulphuric acid dissolves **chlorine,** and also **bromine;** and R. Weber said that **iodine** is only slightly soluble in conc. sulphuric acid. R. H. Adie observed that when iodine is heated with conc. sulphuric acid, the iodine is distilled off at 92° without chemical action. G. Gore observed that anhydrous **hydrogen fluoride** mixes quietly with conc. sulphuric acid at −29° to −18°; and L. Pfaundler observed that gaseous hydrogen fluoride is absorbed by conc. sulphuric acid, and when the soln. is heated, the hydrogen fluoride is driven off unchanged. In aq. soln., W. Traube and E. Reubke observed that a mixture of 62 per cent. **hydrofluoric acid,** and 94 per cent. sulphuric acid furnishes fluosulphonic acid, and that there is a state of equilibrium in the soln.: $H_2SO_4+HF \rightleftharpoons F.HSO_3+H_2O$. According to H. Beckurts and R. Otto, chlorosulphonic acid is formed when **hydrogen chloride** is passed into fuming sulphuric acid. R. Behrend noticed the reverse change. V. Cupr studied the absorption of hydrogen chloride by sulphuric acid. The action of sulphuric acid on **chlorides** is a reversible reaction: $H_2SO_4+2MCl = M_2SO_4+2HCl$, or $H_2SO_4+MCl = MHSO_4+HCl$. With hot fuming sulphuric acid, rich in sulphur trioxide, H. Rose said that chlorine and sulphur dioxide may be formed—*vide infra,* sulphur oxychlorides. A. J. Balard observed that conc. sulphuric acid decomposes **hydrobromic acid** into sulphur dioxide, water, and bromine. When the dil. acid acts on a **bromide,** hydrobromic acid is set free, and E. Léger and others have used the method for preparing hydrobromic acid. F. T. Addyman found that there is no decomposition with 30 per cent. H_2SO_4; with 75 per cent. H_2SO_4, only 0·64 per cent. of the hydrogen bromide is decomposed; while with the mol. proportion $H_2SO_4 : KBr = 1 : 2$, 3·22 per cent. of the hydrogen bromide was decomposed, and with the ratios 1 : 1, 1 : 2, and 1 : 3, respectively 8·3, 19·88, and 31·30 per cent. of the hydrogen bromide was decomposed. K. Proskouriakoff found that hydrobromic acid is oxidized by sulphuric acid at

	169°	100°	46°	35°
H_2SO_4	60	70	80	90 per cent.

J. L. Gay Lussac observed that conc. sulphuric acid decomposes **hydrogen iodide,** or an aq. soln. **hydriodic acid,** forming sulphur dioxide, iodine, and water, while with dil. sulphuric acid there is no decomposition. Similarly also with the **iodides,** which, with conc. sulphuric acid, are decomposed: $2KI+3H_2SO_4=2KHSO_4+I_2+SO_2+2H_2O$. The reactions were studied by D. Vitali, F. Bush, and A. Dupasquier. K. Proskouriakoff observed the temp. at which sulphuric acid oxidizes hydriodic acid, and found this occurs at

	100°	60°	50°	45°	36°
H_2SO_4	25	30	35	40	50 per cent.

J. L. Gay Lussac, and J. Kolb stated that the **hypochlorites** are decomposed by sulphuric acid, forming hypochlorous and hydrochloric acids, and some chlorine through the decomposition of the hypochlorous acid. N. A. E. Millon found that conc. sulphuric acid at —18° dissolves 20 vols. of **chlorine dioxide,** forming a yellow soln. which decomposes between 10° and 15° giving off chlorine and oxygen, and forming perchloric acid; at 15° to 20°, 100 c.c. of 99 per cent. H_2SO_4 dissolve 1·54 grms. of **iodine dioxide,** and a more diluted acid dissolves more dioxide; cold dil. sulphuric acid slowly decomposes the dioxide, forming iodine and iodic acid—the reaction is hastened by raising the temp. A. B. Lamb and A. W. Phillips studied the action of sulphuric acid on **iodine pentoxide.** The action of sulphuric acid on chloric acid has been previously discussed, **2.** 19, 12; and similarly also **bromic acid,** and **iodic acid.** A soln. of, say, 120 grms. of iodic acid in 60 c.c. sulphuric acid—the so-called *iodatosulphuric acid*—has been used as an absorbent for carbon monoxide in gas masks. This subject was studied by M. Guillemard and A. Lührmann, A. Desgrez and M. Guillemard, E. Tassilly, and E. Dinoire. S. Smith observed that at 338° the action of potassium chlorate on conc. sulphuric acid is entirely unattended by explosive violence, the addition of the powdered salt to the boiling acid merely resulting in a brisk effervescence, with the production of chlorine, oxygen, and perchloric acid. The volume of oxygen evolved corresponds with about 90 per cent. of the total oxygen contained in the potassium chlorate, whilst the amount of perchloric acid formed is very small. At temp. between 338° and 200° no crackling or detonation is produced. At 170°, however, the addition of potassium chlorate to sulphuric acid results in a number of small detonations, which increase in violence as the sulphuric acid is cooled and reach a maximum between 130° and 120°, when a sharp explosion results. Below 120° the violence of the action diminishes, until, at 60°, chlorine peroxide is quietly evolved without cracking or detonation. The first action of the acid probably forms the anhydride, Cl_2O_5, and this at once decomposes into chlorine and oxygen; the oxygen oxidizes the chlorine to perchlorate so that, as W. Ramsay emphasized, the equation: $3KClO_3=KClO_4+K_2O+2ClO_2$, must be indeterminate. F. von Stadion, and G. S. Sérullas said that the **perchlorates** are not decomposed at temp. below 100° by conc. sulphuric acid; while C. Langlois, C. F. Rammelsberg, and C. G. Lautsch showed that **periodic acid** and the **periodates** are decomposed by conc. sulphuric acid.

F. C. Vogel[4] showed that when conc. sulphuric acid is heated with **sulphur,** sulphur dioxide is formed. R. H. Adie observed that sulphur dioxide appears at 200°, and no hydrogen sulphide is formed. F. C. Vogel said that when **hydrogen sulphide** is passed into sulphuric acid, water is formed as well as some sulphurous acid and sulphur, but when the acid is diluted with 4 vols. of water, no reduction occurs. According to A. F. de Fourcroy and L. N. Vauquelin, when **sulphur dioxide** is passed into well-cooled sulphuric acid, no hyposulphurous acid is formed, but the frozen mass evolves sulphur dioxide when thawed. According to A. Bussy, when sulphuric acid is agitated with liquid sulphur dioxide, only a little of the latter dissolves in the former; most of the sulphur dioxide forms a layer above the sulphuric acid. H. Rose described a liquid which he regarded as a compound $2SO_3.SO_2$, formed by passing sulphur dioxide into anhydrous sulphuric acid. The product evaporates rapidly in air, forming a thick cloud; it effervesces violently with water giving off sulphur dioxide; and it forms a yellow mixture of sulphite and sulphate when treated with ammonia. It is doubtful if H. Rose's product was anything more than a soln. of the gas in sulphuric acid—*vide supra,* the solubility of sulphur dioxide in sulphuric acid. V. Cupr studied the absorption of sulphur dioxide by sulphuric acid. J. W. Döbereiner said that the reduction occurs only with fuming sulphuric acid. A. Geuther observed that **carbon disulphide** is miscible with sulphuric acid free from water, while M. Brault and A. B. Poggiale said that the cold acid decomposes carbon disulphide, forming carbon and sulphur, and when the mixed vapours are passed through a red-hot tube, sulphur, hydrogen sulphide, sulphur dioxide, and carbon monoxide are formed. According to H. Rose, N. W. Fischer, E. Moles, and A. Hilger, **selenium** and **tellurium** dissolve in conc. sulphuric acid, forming a green or a red soln; part of the metalloid is oxidized and some sulphur dioxide is formed. R. H. Adie observed that when selenium is heated with sulphuric acid, sulphur dioxide appears at 170°, and no hydrogen sulphide is formed.

A. Christoff,[5] and C. Bohr measured the solubility of **nitrogen** (*q.v.*) in sulphuric acid. Sulphuric acid and aq. **ammonia** form salts—ammonium sulphates; E. C. Franklin and C. A. Kraus found that the acid is very slightly soluble in liquid ammonia. J. D. van der Plaats observed that **hyponitrous acid** is decomposed by conc. sulphuric acid, forming nitrous oxide. According to A. H. Allen, **nitric oxide** is absorbed by conc. sulphuric acid, and not by acid diluted in the proportion 3 : 2; according to G. Lunge, the gas is not absorbed by the dil. acid, but this is wrong. He found that 100 c.c. of 96 per cent. sulphuric acid dissolved 3·5 c.c. of nitric oxide; and 60 per cent. acid, 1·7 c.c. of gas. T. Bayley showed that the gas is more soluble if the sulphuric acid contains a trace of mercury or other metal salt, and F. Nettlefold added that only impure nitric oxide is dissolved by conc. sulphuric acid. O. F. Tower measured the solubility of the gas in the acid. A. Graire observed that sulphuric acid is reduced by nitric oxide—*vide supra,* the theory of the lead chamber process for sulphuric acid; and **8**. 49, 35, nitric oxide. The action of **nitrogen peroxide** on sulphuric acid was discussed by R. Weber, C. A. Winkler, C. W. Hasenbach, and G. Lunge and E. Weintraub—*vide* **8**. 49, 64, and the theory of the lead chamber process. A. Sanfourche and L. Rondier measured the press. developed by mixtures of **nitrous acid** and sulphuric acid. The observations of J. Kolb, and A. V. Saposchnikoff and others on the physical properties of mixtures of **nitric acid** and sulphuric acid have been discussed in connection with the former acid. Sulphuric acid abstracts water from nitric acid, and makes it more active for nitrating compounds. A. Marshall questions this; but C. D. Carpenter and A. Lehrman observed that sulphuric acid dehydrates nitric acid even in the presence of enough water to form $H_2SO_4.H_2O$. The observations of J. Kendall, W. C. Holmes, A. V. Saposchnikoff, W. B. Markownikoff, C. D. Carpenter and A. Lehrman, etc., on the action of sulphuric acid on nitric acid have been discussed in connection with nitratosulphuric acid—**8**. 49, 63—so also have the binary system: H_2SO_4–HNO_3; and the ternary system: HNO_3–H_2SO_4–H_2O. A. V. Saposchnikoff said that conc. nitric acid does not form a compound with conc. sulphuric acid, as supposed by W. B. Markownikoff, but with an excess of sulphuric acid, the soln. may contain a little nitrogen pentoxide. A. Sanfourche and L. Rondier measured the press. developed by mixtures of nitric and sulphuric acids.

J. Pelouze[6] observed no change with red **phosphorus** and sulphuric acid in the cold, but when heated, sulphur dioxide and phosphoric acid are formed. When phosphorus and conc. sulphuric acid are heated in a sealed tube, A. Oppenheim said that the reaction can be symbolized: $3H_2SO_4+2P=2H_3PO_3+3SO_2$. When phosphorus is heated in boiling sulphuric acid, in a capacious flask, it burns in the acid vapour, with the separation of sulphur; H. Rose said that **phosphine** slowly reduces sulphuric acid at ordinary temp., forming phosphoric acid, sulphur, and sulphur dioxide. According to A. Geuther, when sulphuric acid is heated with

phosphorus trichloride, the reaction can be symbolized: $2H_2SO_4+PCl_3=ClHSO_3+SO_2+HPO_3+2HCl$. C. Gerhardt and L. Chiozza observed that conc. sulphuric acid reacts with **phosphorus pentachloride**, forming sulphur trioxide and phosphoryl chloride; while A. W. Williamson showed that chlorosulphonic acid is first produced, then sulphuryl chloride, and phosphoryl chloride, while if the temp. exceeds 145°, some phosphorus dioxychloride, PO_2Cl, is produced. P. N. Raikow found that sulphuric acid dissolves in syrupy **phosphoric acid** at ordinary temp., and when the mixture is heated to 350°, sulphur dioxide is given off. A. Prinvault observed that sulphatophosphates are produced when conc. sulphuric acid is heated with the **alkali phosphates.** R. H. Adie found that when sulphuric acid is heated with **arsenic,** sulphur dioxide appears at 110°; with **antimony,** at 90°–95°; and with **bismuth,** at 90°—in no case was hydrogen sulphide observed.

When **carbon**—charcoal—is heated with conc. sulphuric acid the reaction can be symbolized: $C+2H_2SO_4=2H_2O+CO_2+2SO_2$, and at a higher temp.—dull redness—carbon monoxide and dioxide, hydrogen, and sulphur are formed. R. H. Adie [7] said that the formation of sulphur dioxide can be detected at 188°, and no hydrogen sulphide is formed. M. Berthelot found that graphite is not attacked at 100°, but retort carbon colours the liquid brown, and wood-charcoal produces small quantities of sulphur and carbon dioxides. A. Verneuil said that metallic acid, pyromellitic acid, and benzenepentacarboxylic acid are produced by the action of conc. sulphuric acid on wood charcoal at 280°–300°. D. Namasivayam, N. Schiloff and S. Pewsner, I. M. Kolthoff, and L. R. Parks and P. C. Bartlett, studied the adsorption of sulphuric acid by charcoal. L. R. Parks and P. C. Bartlett, and M. Dubinin studied the adsorption of sulphuric acid by carbon. J. Thoulet studied the attraction between a dissolved solid and a substance immersed in the soln, applied to the case of lignite and sulphuric acid. C. Bohr measured the solubility of **carbon dioxide** (*q.v.*) in sulphuric acid; and A. Christoff, of **carbon monoxide** (*q.v.*). J. Milbauer found that at 250° sulphuric acid is reduced by carbon monoxide: $H_2SO_4+CO=CO_2+SO_2+H_2O$, so long as the conc. of the acid does not fall below 91 per cent. H_2SO_4, and it is accelerated by the presence of certain catalysts—*e.g.* palladium, iridium, mercury, selenium, silver, gold, and tin—but not by platinum, osmium, and copper sulphate. Sulphuric acid corrodes many organic substances and colours them brown. In 1661, R. Boyle thus described the reducing action of **turpentine:**

> Suspecting the common oyle of vitrioll not to be altogether such a simple liquor as chymists presume it, I mingled it with an equal or a double quantity (for I tryed the experiment more than once) of common oyle of turpentine, such as together with the other liquor I bought at the drugsters. And having carefully (for the experiment is nice, and somewhat dangerous) distilled the mixture in a small glass retort, I obtained according to my desire (besides the two liquors I had put in) a pretty quantity of a certaine substance, which sticking all about the neck of the retort discovered itself to be sulphur, not only by a very strong sulphureous smell, and by the colour of brimstone; but also by this, that being put upon a coal, it was immediately kindled, and burned like common sulphur. And of this substance I have yet by me some little parcells, which you may command and examine when you please. So that from this experiment I may deduce either one, or both of these proportions, that a real sulphur may be made by the conjunction of two such substances as chymists take for elementary, and which did not either of them apart appear to have any such body in it; or that oyle of vitrioll though a distilled liquor, and taken for part of the saline principle of the concrete that yeelds it, may yet be so compound a body as to contain, besides its saline part, a sulphur like common brimstone, which would hardly be itself a simple or uncompounded body.

A. Christoff found that at 20°, one c.c. of 95·6 per cent. sulphuric acid absorbs 0·03303 c.c. of **methane;** 61·62 per cent. H_2SO_4, 0·01407 c.c.; and 35·82 per cent. H_2SO_4, 0·01815 c.c. R. A. Worstall said that fuming sulphuric acid will attack the aliphatic and aromatic hydrocarbons. Thus, although the cold fuming acid is without action on hexane, heptane, or octane at ordinary temp., these compounds are sulphonated by the acid at their b.p. S. G. P. Plant and N. V. Sidgwick said that there are three successive stages in the absorption of **ethylene** by sulphuric acid:

(i) a dissolution of the gas in the liquid; (ii) a reaction: $C_2H_4+H_2SO_4=C_2H_5.HSO_4$; and (iii) a further reaction with the acid to form ethyl sulphate, $(C_2H_5)_2SO_4$. The second and third reactions may be simultaneous, and they proceed at rates proportional to the products of the concentrations of the sulphuric acid and ethylene in the one case and ethyl hydrosulphate in the other. A. Damiens showed that cupric oxide or sulphate catalyzes the reaction, and that there is a state of equilibrium: $H_2SO_4+(C_2H_5)_2SO_4 \rightleftharpoons 2C_2H_5(HSO_4)$. The reaction was studied by W. Lommel and R. Engelhardt, and W. Gluud and G. Schneider. S. G. P. Plant and N. V. Sidgwick said that **propylene** is absorbed more readily than ethylene, but the reactions are more complex, for besides propyl sulphate and hydrosulphate, a colourless oil, free from sulphur, and probably a mixture of secondary alcohols, is formed. J. U. Nef claimed that **butylene** and the higher olefines were quantitatively converted into polymers by conc. sulphuric acid at 0°, while propylene remained dissolved in the acid as propyl sulphate. A. Michael and co-workers found that **isobutylene**, $(CH_3)_2C=CH_2$, is rapidly and completely dissolved by 63 per cent. sulphuric acid at 17°, while **tetramethylethylene,** $(CH_3)_2C=C(CH_3)_2$, reacts completely with 77 per cent. acid at ordinary temp., but not so rapidly as amylene, $(CH_3)_2C=CH.CH_3$. The amylene, $(C_2H_4)(CH_3)C=CH_2$, dissolves more readily in 66 per cent. acid than does the amylene $(CH_3)_2CH.CH=CH_2$. A. Wischnegradsky obtained large yields of amyl alcohol by the action of cold, conc. sulphuric acid on amylene. W. R. Ormandy and E. C. Craven, and B. T. Brooks and I. Humphrey studied the action of sulphuric acid on various **olefines** –β-methyl-α-butene, β-methyl-α-pentene, α-hexene, methylcyclohexene, iso-α-heptene, γ-heptene, γ-ethyl-β-pentene, tetramethylethylene, α-octene, α-isoctene, β-methyl-β-undecene, hexadecene, menthene, styrene, as well as the terpenes, α-pinene, β-pinene, limonene, and myrcene. In agreement with A. Michael and R. F. Brunel, they found that the tendency of the aliphatic olefines to form alkyl sulphates and alcohols increases with increasing mol. wt., and approaches a maximum with the amylenes and hexene. The substitution of electronegative radicles—*e.g.* hydroxyl, carboxyl, or the halogens—for hydrogen makes the olefines more resistant towards sulphuric acid. Tetramethylethylene is more reactive than its isomer α-hexene. This is attributed to the fact that the unsaturated tetradic C : C-group in α-hexene has three of its valencies taken up by hydrogen, whereas in tetramethylethylene, the hydrogen atoms are replaced by the more electropositive CH_3-groups. The olefines of higher mol. wt. are inclined to polymerize when treated with sulphuric acid, and the polymerides still containing at least one double bond resist attack by sulphuric acid better than the parent olefine. Thus duodecene, $C_{12}H_{24}$, is almost quantitatively converted into the dipolymer, $C_{24}H_{48}$. There is no evidence of ring formation. If amylenes, hexenes, or heptenes are treated with 85 per cent. sulphuric acid, below 15°, alcohols are formed but not necessarily by the formation and subsequent hydrolysis of the alkyl sulphate. R. P. Anderson and C. J. Engelder observed that fuming sulphuric acid has a solvent action on the **gasolene** vapours in natural gas. Conc. sulphuric acid was found by M. Berthelot, S. Zeisel, and W. Muthmann to absorb slowly **acetylene**, forming a sulphonic acid. M. Berthelot, and H. I. Lagermarck and A. P. Eltekoff said that with a boiling soln. of sulphuric acid (3 : 7) acetaldehyde is formed, and, according to H. Erdmann and P. Köthner, with a more conc. acid (2 : 1) crotonaldehyde is formed. The chemical action was discussed by G. Schröter, etc. According to A. Michael and A. Adair, when conc. sulphuric acid is boiled for 20–30 hrs. with **benzene,** some benzoylsulphonic acid is formed. The reaction was studied by G. Monselise, L. B. von Barthenau and C. Senhofer, C. Senhofer, G. Heinzelmann, W. Egli, M. Berthelot, etc.

The esterification of **methyl alcohol** by sulphuric acid was discussed by R. Kremann and H. Neumann,[8] and J. Guyot and L. J. Simon; and of **ethyl alcohol** by sulphuric acid by A. Villiers, F. W. Bushong, D. McIntosh, H. Meyer, R. Kremann, P. N. Evans and co-workers, and A. Zaitschek. B. T. Brooks and I. Humphrey found that **allyl alcohol** reacts with the 60 per cent. acid to form allyl hydrosulphate, and **cinnamic alcohol** is polymerized by the 85 per cent. acid at 0°, and similarly also with **cinnamic aldehyde,** eugenol, *iso*eugenol, and safrol. R. Kremann and H. Hönel studied the velocity of the reaction with **acetone** resulting in the formation of mesityl oxide; and D. McIntosh, the formation of oxonium compounds. The effect of sulphuric acid on **ether** has been studied by A. W. Porter, and J. R. Pound; and on *p*-totyl ethyl ether, by P. R. Roberts and G. Alleman. C. Mauguin and L. J. Simon represented the reaction of sulphuric acid on **carbon tetrachloride** at 150° by the equation: $CCl_4+H_2SO_4=HClSO_3+COCl_2+HCl$, and $2HClSO_3+CCl_4=S_2O_5Cl_2+2HCl+COCl_2$. V. V. Tschelinceff and N. A. Kozloff, E. Archibald and D. McIntosh, D. McIntosh, A. Hantzsch, and G. Oddo and E. Scandola found that sulphuric acid reacts with ethers to form compounds which, from their analogy with the substituted ammonium compounds, can be regarded as oxonium derivatives. The action of sulphuric acid on various **organic acids** has been studied by F. W. O. de Coninck and M. Raynaud, B. T. Brooks and I. Humphrey, J. van Peski, M. Bergmann and F. Radt, J. Kendall and C. D. Carpenter, J. Milbauer and A. Nemec, etc. A. Lehrman studied the ternary system: acetic and sulphuric acids and water. J. A. Christiansen observed that the decomposition of oxalic acid by sulphuric acid is retarded by the presence of a small proportion of water, probably in consequence of the displacement of the equilibrium $H_2SO_4 \rightleftharpoons SO_3+H_2O$, since the addition of sulphur trioxide greatly increases the rate of the reaction. Observations on the aromatic **disulphides** were made by S. Smiles and co-workers; on aromatic **disulphoxides,** by T. P. Hilditch; on **nitroheptane,** by R. A. Worstall; on **nitrobenzene,** by M. L. Crossley and C. B. Ogilvie; on malic acid, by E. L. Whitford; on various organic compounds—aldoses, dicarboxylic acids, amino-acids, α- and β-naphthol, and dihydroxybenzenes—by J. Milbauer and A. Nemec; and on **ferrocyanides,** by P. Chrétien. The formation of carbon monoxide (*q.v.*) by the action of sulphuric acid on **potassium ferrocyanide** was investigated by J. W. Döbereiner, J. J. Berzelius, G. Fownes, M. Merk, T. Everitt, C. G. Wittstein, H. Aschoff, A. W. Williamson, and R. H. Adie and K. C. Browning. P. G. Kronacker studied the conversion of the nitrogen of the **amino-acids** into ammonium sulphate by the action of 66 per cent. sulphuric acid, with and without potassium permanganate and mercury. E. J. Mills and J. Takamine, and J. Walker and J. R. Appleyard studied the absorption, etc., of the acid by **silk;** E. J. Mills and J. Takamine, W. W. Paddon, and D. Vorländer and A. J. Perold, by **wool;** E. J. Mills and J. Takamine, by **cotton;** S. G. Mokrushin, by **filter-paper;** and J. A. Wilson, and V. Kubelka and J. Wagner, by **leather.** The action of sulphuric acid on **glass** (*q.v.*) has been discussed by F. R. Weber and E. Sauer,[9] etc.; on various **silicates** (*q.v.*) by J. Hazard, etc.

The effects of sulphuric acid on the different **metals** are discussed in connection with the individual elements. St. von Bogdandy and M. Polanyi[10] studied the emission of ions when sulphuric acid attacks sodium vapour. General observations have been made by C. H. Sluiter, R. H. Adie, C. M. van Deventer, M. J. Fordos and A. Gélis, A. Ditte, and M. Berthelot. In some cases, dependent on the conc. of the acid, the nature of the metal, and the temp., hydrogen, hydrogen sulphide, sulphur dioxide, and sulphur or the metal sulphide may be formed. G. J. Burch and J. W. Dodgson observed that with conc. sulphuric acid, at 16°, sodium, weighted with a glass rod, is less rapidly attacked than by water; the action is moderate and bubbles of gas are steadily given off. Contact of the sodium with another metal usually retards the action—aluminium and magnesium accelerate the action, so much that the sodium quickly inflames; platinum, iron, and carbon retard the action. The sodium remains clean and bright while the gas comes from the surface of the other metal. According to T. L. Phipson, when a piece of sodium is placed in sulphuric acid of sp. gr. 1·845, sodium sulphide is the chief product of the action. R. Pictet observed that below —68° potassium does not react with 35 per cent. sulphuric acid; and sodium not below —50°. P. Neogi and R. C. Bhattacharyya found that sulphates are not attacked by magnesium amalgam. P. D. Schenck discussed metals for resisting the action of sulphuric acid. Lead is in common use for up to 95 per cent. cold acid, and up to 80 per cent. hot acid; aluminium bronzes and copper-silicon-manganese bronzes resist cold soln. with up to about 40 per cent. sulphuric acid; high nickel copper alloys, chrome-nickel steels, and nickel-silicon steels behave like the bronzes. The high silicon irons have been used for resisting all concentrations and temperatures of sulphuric acid, but they are difficult to work. K. C. Sen observed that the adsorptions of sulphuric acid by hydrated **chromic oxide, aluminium oxide,** and **ferric oxide** in millieq. per gram from acid with 1·1320 millieq. per 100 c.c. are respectively 4·273, 1·793, and 1·696.

The action of sulphuric acid on the **bases** results in the formation of **sulphates**—*e.g.* K_2SO_4, $CaSO_4$, $Fe_2(SO_4)_3$, etc.; of bisulphates or **hydrosulphates**—*e.g.* $KHSO_4$, $CaHSO_4$, etc.; of **pyrosulphates**—*e.g.* $Na_2S_2O_7$, etc.; of various other *acid sulphates*—or **polysulphates**[11]—*vide* **2.** 20, 26—and of *basic sulphates* or **oxysulphates**[12]—*vide* copper sulphates, etc. Many **complex sulphates** or *double and triple sulphates* have been reported;[13] and a number of **heteropoly-acids** have been discussed—*e.g.* A. Recoura's,[14] E. Baud's ferrisulphuric acid, chromisulphuric acids, etc. Excepting the pyrosulphates, these compounds are discussed in connection with the individual elements. G. C. A. van Dorp[15] studied the ternary systems: Li_2SO_4–H_2SO_4–H_2O, $(NH_4)_2SO_4$–H_2SO_4–H_2O, and the quaternary system: $(NH_4)_2SO_4$–Li_2SO_4–H_2SO_4–H_2O; H. W. Foote the ternary systems: Na_2SO_4–H_2SO_4–H_2O, and RSO_4–H_2SO_4–H_2O, where R represents the bivalent elements, Fe, Cu, Ba, Ca, Be, and the quaternary system Na_2SO_4–$CuSO_4$–H_2SO_4–H_2O; and A. D. Donk, the ternary system: $PbSO_4$–H_2SO_4–H_2O.

The physiological action of sulphuric acid.—F. C. Calvert[16] said that a soln. 1 : 1000 does not affect protoplasmic life or fungi. Sulphuric acid is poisonous to man, and a fatal case of the poisoning of an adult by 3·8 grms. of acid was reported by R. Christison, and this is the smallest lethal dose on record. When externally applied, the conc. acid may produce phenomena resembling scalds or burns; the destruction of the tissue may not be deep seated if the acid is quickly washed off. The skin is at first coloured white, and at a later period brown, and part may appear as if it had been dissolved. When administered internally, there is immediate and great suffering; the tongue and throat swell and inflame so that saliva cannot be swallowed. The acid attacks the mucous membrane of the gullet, and stomach. There may be excessive vomiting and retching. Pieces of mucous membrane may be expelled. The bowels are usually constipated, and the urine contains an excess of sulphates and often albumen with hyaline casts of uriniferous tubes. The pulse is small, the breathing slow, the extremities may be affected with convulsions and cramps, and death may follow in 24–36 hrs., or be more protracted and painful. In bad cases, the sulphuric acid may dissolve the stomach and pass into the peritoneum producing effects like a penetrating wound in the abdomen. In chronic poisoning by small doses W. Starkoff showed that it acts as a specific poison on the blood. R. Kobert mentioned that drunkards addicted to Schnapps may show symptoms of chronic poisoning because this liquor is acidified with sulphuric acid to give it a sharp taste. H. Weiske found that lambs, given small doses of the acid for six months, grew thin, and their bones—excepting the long bones and those of the head—were deficient in lime salts; and the muscles have an abnormally low proportion of these salts. N. Sieber, P. Miquel, and C. T. Kingzett observed that dil. sulphuric acid hinders putrefaction, and acts as an antiseptic; and W. O. von Leube said that a very dil. soln. has been sold under the commercial name *kreosozon* for use in preserving foods. M. M. Hayduck found that the dil. acid has a detrimental effect on the development of yeast.

Some uses of sulphuric acid.—In 1920, the world's production of sulphuric acid of a sp. gr. of about 1·72 downwards approximated 5 million metric tons, and of this, about three-fourths was used for making fertilizers, ammonium sulphate, and other artificial manures. This *dilute acid* is also used for making salt-cake and hydrochloric acid, and indirectly for soda-ash, bleaching powder, etc. It is used in the preparation of many acids—*e.g.* hydrofluoric, sulphurous, nitric, phosphoric, boric, chromic, oxalic, tartaric, citric, acetic, and stearic acids; it is used in manufacturing phosphorus, iodine, bromine, and numerous sulphates—*e.g.* barium sulphate or *blanc fixé*, the alkali sulphates, alums, and the sulphates of the metals—potassium dichromate, ethers, organic colouring matters, starch, syrup, sugar, etc. It is employed in the metallurgy of copper, silver, cobalt, nickel, platinum, etc. It is used for pickling or cleaning sheet-iron, to be galvanized or tinned. It is used in making parchment paper, for the saccharification of corn, for effervescent drinks and mineral waters, in the preparation of tallow, in the recovery of fatty acids from soap suds, for destroying vegetable fibres in mixed fabrics, in making artificial silk, and generally in dyeing, calico printing, tanning, refining mineral oils, rubber refining, in making glycerol, vegetable oils, glue, gelatine, size, weed-killers, etc. It is employed as a chemical reagent in innumerable cases; it is used in some galvanic cells; as a medicine against lead-poisoning, etc. It is used admixed with potassium dichromate as an oxidizing agent. The *concentrated acid* is used in purifying colza oil, benzene, petroleum, paraffin, and other mineral oils, in manufacturing fatty acids, organosulphonic acids, indigo, nitrocompounds and nitric ethers, nitroglycerol, nitrocellulose, nitrobenzene, picric acid, nitrotoluene, etc. It is used for drying air and gases, for producing ice by the rapid evaporating of water, in vacuo; for refining gold and silver, describing copper, etc. The *fuming acid* is used in manufacturing some organosulphonates—used in making alizarine, eosine, indigo, etc. It is used in making explosives; purifying ozokerite, making shoe-blacking, and in revivifying the spent acids from the manufacture of nitrotoluene, nitrocellulose, etc. This subject is discussed in more detail in J. W. Parke's *The Concentration of Sulphuric Acid* (London, 356, 1924).

Some reactions of analytical interest.—P. Harting[17] said that sulphuric acid will redden **litmus** when only one part is present in 25,000 parts of water—or in 62,500 parts during an hour—*vide supra*, electrometric titration. Dil. soln. of sulphuric acid give no precipitate with dil. soln. of a **silver salt,** but with conc. soln. white crystals of silver sulphate may be deposited. A white precipitate is produced when even dil. soln. of sulphuric acid are treated with **barium chloride.** P. Harting said that the white precipitate is produced with one part of barium salt in 79,300 parts of water; T. G. Wormley said 1 : 21540; C. R. Fresenius, 1 : 23,100 to 25,200; and F. Jackson, 1 : 256,000. J. L. Lassaigne found that a soln. of potassium sulphate with one part of sulphuric acid in 50,000 parts of water gives a feeble turbidity with barium nitrate and a very feeble one with lead nitrate, with 1 : 100,000 the former gives a very feeble turbidity and the latter none; with 1 : 200,000 barium nitrate gives a feeble turbidity in 15 minutes; and with 1 : 400,000 none. J. W. Mellor has discussed the difficulties associated with the quantitative precipitation of barium sulphate in the analysis of sulphates—see also **3.** 24, 16. A similar precipitate of strontium sulphate is produced with a **strontium salt** under conditions when the product with a thiosulphate is soluble. F. Jackson said that the precipitate with a strontium salt is sensitive to 1 : 8000, and with a **calcium salt,** to 1 : 2000—P. Harting gave 1 : 310, for the calcium salt, and 1 : 5000 for a lead salt, whereas F. Jackson gave 1 : 16,000 for the **lead salt.** According to G. Denigès, the presence of the sulphuric ion in insoluble sulphates, such as those of lead, mercurous mercury, calcium, strontium, and barium, may readily be shown by adding to the sulphate a 10 per cent. soln. of mercuric nitrate in nitric acid (1 in 100). Turpeth mineral is formed, and may be detected, if necessary, microscopically. Calcium and mercurous sulphates give the reaction immediately in the cold, strontium and lead sulphates only slowly, and barium sulphate only on boiling. F. Jackson said that with **mercurous salts** a precipitate is produced with one part of the acid in 1000 parts of soln. According to G. von Knorre, a soln. of **benzidine** in dil. hydrochloric acid gives a white, crystalline precipitate of benzidine sulphate in neutral and acid soln. of sulphates in the presence of ferrous, copper, cobalt, zinc, nickel, manganese, and aluminium compounds. Ferric and chromic salts should be reduced before the benzidine is added.

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§ 32. Pyrosulphuric Acid and the Pyrosulphates

The chemical individuality of solid **pyrosulphuric acid,** $H_2S_2O_7$, is confirmed by the f.p. curve, Fig. 77; by the analyses of J. C. G. de Marignac,[1] A. C. Schultz-Sellack, and R. Weber ; and by the existence of a series of salts. The constitution of the acid was discussed in connection with sulphuric acid from which it appears that the ordinary acid is to be regarded as a meta-compound, say **metadisulphuric acid.** The impure acid associated with more or less sulphur dioxide, or even pyrosulphuric acid itself, is included among the **fuming sulphuric acids** (*q.v.*).

Pyrosulphuric acid is formed when incompletely dehydrated ferrous sulphate or sodium pyrosulphate is heated to redness : $4FeSO_4+H_2O=H_2S_2O_7+2SO_2+2Fe_2O_3$. A. C. Schultz-Sellack made it by mixing fused sulphur trioxide with the correct proportion of sulphuric acid. J. C. G. de Marignac said that this acid crystallizes from conc. fuming sulphuric acid at ordinary temp., or, according to E. Mitscherlich, at 0°. After many recrystallizations, the crystals were found by J. C. G. de Marignac, and A. C. Schultz-Sellack to melt at 35° ; R. Auerbach gave 32·55° ; and R. Knietsch, 36° for the m.p.—*vide* Fig. 77. R. Auerbach found the mean sp. ht. of the liquid to be 0·294 ; the heat of fusion 17·9 Cals. ; and the mol. lowering of the f.p. 10·5°. According to A. C. Schultz-Sellack, the dry crystals do not exert an appreciable vap. press. of sulphur trioxide, and are not decomposed by dry air. The molten acid is very liable to undercooling, but the undercooled liquid, at ordinary temp., does show an appreciable vap. press. of the anhydride ; and at a higher temp. it dissociates into sulphur trioxide and sulphuric acid. This indicates that the acid dissociates when fused. J. Thomsen gave 26·9 Cals. for the heat of soln. of $\frac{1}{2}H_2S_2O_7+1600H_2O$. In the electrolysis of pyrosulphuric acid with aluminium electrodes with a current of 200 volts and 200 ohms external resistance, B. G. Cobb found that when the current was cut off, and the apparatus was placed in the dark, sulphur trioxide is disengaged in the cold and, unlike the case with sulphuric acid (*q.v.*), sparking ceased after 14 minutes. For the alleged hydrates of pyrosulphuric acid, *vide supra*, the hydrates of sulphuric acid.

A. C. Schultz-Sellack found that selenium dissolves in pyrosulphuric acid and is at the same time slightly oxidized, the green soln. gradually turns yellow. Tellurium behaves similarly, forming a red soln. which gradually turns brown. According to E. Divers and T. Shimidzu, copper and mercury dissolve in pyrosulphuric acid when the mixture is treated with water, the sulphates are precipitated, and the liquid holds sulphur dioxide in soln.; copper forms cuprous sulphide and some cupric sulphate; tin produces a blue soln. presumably owing to the formation of the hemitrioxide and stannous sulphate. The blue colour is discharged when the liquid is diluted. For other properties, *vide* fuming sulphuric acid.

H. Rose[2] found that powdered ammonium sulphate slowly absorbs a little vapour of sulphur trioxide, forming a product which melts when heated, and then decomposes like ammonium hydrosulphate (*q.v.*). H. Schulze made **ammonium pyrosulphate,** $(NH_4)_2S_2O_7$, by treating ammonium sulphate with liquid sulphur trioxide and afterwards driving off the excess of trioxide by warming the product on a water-bath; he also prepared the same compound by the action of chlorosulphonic acid on ammonium sulphate: $ClHSO_3+(NH_4)_2SO_4=(NH_4)_2S_2O_7+HCl$. The product was heated to drive off the excess chlorosulphonic acid, but not enough for fumes of sulphur trioxide. The cooling of the molten mass furnishes a crystalline mass which is never quite free from chlorine. This method was used by H. Schiff for the potassium salt. Ammonium pyrosulphate cannot be prepared by heating the hydrosulphate, though the method is applicable to the alkali pyrosulphates, although J. Baum found that if the ammonium hydrosulphate be heated in vacuo to 260°–320°, it forms the pyrosulphate—at atm. press., the pyrosulphate would decompose. Ammonium pyrosulphate can be melted without decomposition, and on cooling it forms a white, crystalline mass; it rapidly deliquesces in air, and the resulting liquor deposits crystals of the hydrosulphate.

According to D. A. Rosenstiehl, **sodium pyrosulphate,** $Na_2S_2O_7$, remains as a residue in the preparation of pyrosulphuryl chloride by the action of anhydrous sulphuric acid on sodium chloride, and M. Dietzenbacher said that this salt occurs in some varieties of commercial fuming sulphuric acid. R. Weber observed that when sodium sulphate is treated with sulphur trioxide above 150°, polysulphates are not formed, and sodium pyrosulphate appears; some pyrosulphate, mixed with sulphate, is also formed when sodium hydrosulphate is heated to 315°, and J. Baum obtained it by heating the hydrosulphate in vacuo at 260°–320°: $2NaHSO_4=H_2O+Na_2S_2O_7$. H. Schulze prepared the salt by the action of an excess of chlorosulphonic acid on sodium sulphate and subsequently distilling off the excess of acid. A. C. Schultz-Sellack said that this salt is formed, accompanied by the hydrosulphate, when a soln. of normal sulphate in fuming sulphuric acid is allowed to crystallize. L. Cambi and G. Bozza said that only direct synthesis from anhydrous sulphates and sulphur trioxide furnishes the pure salts. The dehydration of the hydrosulphate does not proceed to completion, even under reduced press., or in a current of sulphur trioxide vapour. Sodium pyrosulphate, continued L. Cambi and G. Bozza, forms lustrous, translucent, white crystals of sp. gr. 2·658 at 25°/4°, and m.p. 400·9°. In moist air, the salt soon forms a conc. soln. of sodium hydrosulphate. A. C. Schultz-Sellack found that at a red-heat sodium pyrosulphate gives off sulphur trioxide, forming the normal sulphate. R. Robl observed no fluorescence with the salt in ultra-violet light. The system $Na_2S_2O_7.H_2O$–$Na_2S_2O_7$, or $(NaHSO_4)_2+$–$Na_2S_2O_7$, is very liable to supercooling. The eutectic at 182·7° contains 6·8 molar per cent. of the pyrosulphate, Fig. 100. The hydrosulphate melts at 185·7°. The pure pyrosulphate, and all mixtures containing it in greater proportion than 10 per cent., are greenish-yellow when liquid. A. C. Schultz-Sellack was unable to prepare *sodium hydrosulphate*, $NaHS_2O_7$.

D. A. Rosenstiehl obtained **potassium pyrosulphate,** $K_2S_2O_7$, as in the analogous case of the sodium salt. A. C. Schultz-Sellack prepared the salt by heating to dull redness a mixture of equimolar parts of potassium sulphate and sulphuric acid. The combination occurs at 400° in a current of air. P. L. Geiger, and V. A. Jacquelain also obtained potassium pyrosulphate by the action of conc. sulphuric acid on potassium sulphate or nitrate. H. Rose said that sulphur trioxide does not unite with potassium sulphate at ordinary temp., but A. C. Schultz-Sellack did not agree with this, he found it better to work at a higher temp., and M. Berthelot recommended 180°. J. Baum obtained the salt as in the analogous case of sodium pyrosulphate; and H. Schiff, by the action of chlorosulphonic acid on the sulphate, or of potassium chlorosulphonate on the hydrosulphate: $KHSO_4+ClKSO_3=HCl+K_2S_2O_7$. A. C. Schultz-Sellack found that potassium pyrosulphate furnishes acicular crystals of sp. gr. 2·277, and m.p. 300°. V. A. Jacquelain gave 210° for the m.p.; while L. Cambi and G. Bozza said that the salt crystallizes in transparent, colourless prisms of sp. gr. 2·512 at 25°/4°, and m.p. 414·2°. On cooling, the solid undergoes a polymorphic transformation from γ-$K_2S_2O_7$ to β-$K_2S_2O_7$ at 315°, Fig. 101, forming an opaque, porcelainic mass; a second transformation from β-$K_2S_2O_7$ to α-$K_2S_2O_7$ can be detected thermally at 225°. The α-form is the stable variety below 225°. Both changes are frequently accompanied by marked undercooling, and usually proceed slowly. The molten salt solidifies to a crystalline mass. V. A. Jacquelain said that the hot, sat., aq. soln. deposits crystals of the salt unchanged, but A. C. Schultz-Sellack could not confirm this statement. L. Cambi and G. Bozza found that the system $K_2S_2O_7.H_2O$–$K_2S_2O_7$, *i.e.* $(KHSO_4)_2$–$K_2S_2O_7$, forms a eutectic at 201·2° and 14 molar per cent. of the pyrosulphate, Fig. 101. The polymorphic transformations of the pyrosulphate in the mixtures may escape detection owing to the sluggishness of the changes at low temp. M. Berthelot found that when the salt is dissolved in water, heat, 1·19 Cals. per mol, is first absorbed, and 5–6 minutes later, heat, 0·58 Cal. per mol, is given off due to the pyrosulphate decomposing into the hydrosulphate. The heat of formation, $(K_2SO_4,SO_3)=13$ Cals.; and the heat of hydrolysis, $H_2O+K_2S_2O_7=2KHSO_4+4{\cdot}30$ Cals. E. Drechsel said that the pyrosulphate reacts with the hydrosulphide, forming hydrosulphate and thiosulphate: $KSH+K_2S_2O_7=K_2S_2O_3+KHSO_4$; with sodium ethoxide, potassium ethyl sulphate is formed. According to A. C. Schultz-Sellack, a soln. of the pyrosulphate in conc., fuming sulphuric acid deposits columnar crystals of **potassium hydropyrosulphate,** KHS_2O_7, which melt at 168°; a crystalline mass is formed when the liquid cools. This salt does not fume in air, and is not decomposed in a current of air.

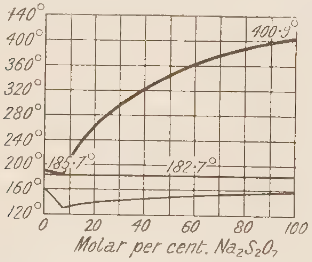

Fig. 100.—Freezing-point Curve of the Binary System: $Na_2S_2O_7$–$(NaHSO_4)_2$.

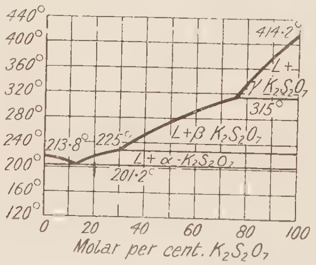

Fig. 101.—Freezing-point Curves of the Binary System: $K_2S_2O_7$–$(KHSO_4)_2$.

According to R. Bunsen, and H. Erdmann, when rubidium hydrosulphate is melted at dull redness, some **rubidium pyrosulphate,** $Rb_2S_2O_7$, is formed; and R. Weber obtained the salt by heating the polysulphate—R. Weber prepared **cæsium pyrosulphate,** $Cs_2S_2O_7$, in a similar manner. R. Weber obtained **silver pyrosulphate,** $Ag_2S_2O_7$, by heating a mixture of molar proportions of silver sulphate and sulphur trioxide in a sealed tube until the mixture had melted. H. Schulze said that the salt can be melted without decomposition. He also prepared **calcium pyrosulphate,** CaS_2O_7, by adding finely-divided calcium sulphate to melted sulphur trioxide. The product is very hygroscopic, and by contact with water produces a hissing noise. The analogous **strontium pyrosulphate,** SrS_2O_7, was prepared in a similar way; and likewise also **barium pyrosulphate,** BaS_2O_7. This salt was obtained by H. Struve by evaporating for crystallization a soln. of 15·89 parts of barium sulphate in 100 parts of fuming sulphuric acid; and by A. C. Schultz-Sellack, by triturating a mixture of the two components, and warming the product up to 150°.

H. Schulze prepared **magnesium pyrosulphate,** MgS_2O_7, by the method used for the calcium salt; and likewise also **zinc pyrosulphate,** ZnS_2O_7. R. Weber prepared **thallous pyrosulphate,** $Tl_2S_2O_7$, by heating the octosulphate to its m.p. H. Schulze prepared **lead pyrosulphate,** PbS_2O_7, as in the case of the calcium salt. H. Ditz and F. Kanhäuser said that probably this salt is present in a soln. of lead sulphate in fuming sulphuric acid. J. J. Berzelius obtained crystals of **uranyl pyrosulphate,** $(UO_2)S_2O_7$, from a sulphuric acid soln. of uranyl sulphate, and A. C. Schultz-Sellack mixed liquid sulphur trioxide with a soln. of uranyl sulphate in an excess of conc. sulphuric acid, and found that after some time small, yellow crystals of uranyl pyrosulphate separate out. The salt is very hygroscopic, and hisses in contact with water. T. Bolas reported **ferrous pyrosulphate,** FeS_2O_7, to be formed when 10 per cent. of a sat. soln. of ferrous sulphate is added to sulphuric acid. As the mixture cools, a white powder is precipitated. This consists of microscopic, prismatic crystals resembling those of Glauber's salt. When exposed to air, the crystals absorb water, forming minute, green, granular crystals resembling ferrous sulphate, but the analysis of which was said to correspond with $FeSO_4.6H_2O$—presumably all had not been hydrated to the heptahydrate. When ferrous pyrosulphate is treated with water, it is converted into heptahydrated ferrous sulphate which then passes into soln.

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§ 33. Polysulphates

Some complex salts of the alkali sulphates and hydrosulphates with sulphuric acid have been previously discussed—**2**. 20, 26. R. Weber[1] prepared **ammonium octosulphate,** $(NH_4)_2O.8SO_3$, or $(NH_4)_2S_8O_{25}$, by heating dry ammonium sulphate and dry sulphur trioxide in a sealed tube. Combination begins at about 100°, and two layers of liquid are formed. If the components be heated in one limb of a Λ-tube, the excess of sulphur trioxide can be distilled from the one limb to the other. R. Weber did not succeed in making *lithium octosulphate*, because of the insolubility of lithium sulphate in molten sulphur trioxide; and similarly with *sodium octosulphate;* but **potassium octosulphate,** $K_2O.8SO_3$, was obtained as in the case of the ammonium salt; but the crystalline product can be more readily purified by pouring off the liquid trioxide, melting the crystals, and again pouring off the liquid from the crystals, and repeating the operation a number of times. The salt melts at about 80°, and it slowly decomposes at the b.p. of sulphur trioxide, forming the pyrosulphate and sulphur trioxide. R. Weber obtained in a similar manner **rubidium octosulphate,** $Rb_2O.8SO_3$, **cæsium octosulphate,** $Cs_2O.8SO_3$, and **thallium pyrosulphate,** $Tl_2S_2O_7$. E. Divers said that these polysulphates are analogous to hydrated salts.

According to W. B. Giles and co-workers, the acid sulphates obtained in the manufacture of hydrochloric, nitric, and acetic acids are capable of combining with more sulphuric, forming **sodium pentasulphate,** $Na_2O.5SO_3.3H_2O$. The dry solid is capable of being transported in ordinary packages—iron drums or kegs. H. Neuendorf also reported polysulphates to be formed by heating alkali hydrosulphates with sulphuric acid. Analogous salts were reported by A. C. Schultz-Sellack, and H. Lescœur. The last-named reported **tetrasulphates** of the type $R_2O.4SO_3.6H_2O$; $3R_2SO_4.H_2SO_4$; and $R_2SO_4.3RHSO_4$; as well as the **trisulphates,** $2R_2SO_4.H_2SO_4$, and the **heptasulphates,** $4R_2SO_4.3H_2SO_4$—*vide* **2.** 20, 26. A. Étard's series of double salts of iron with aluminium, chromium, or manganese, or of chromium with aluminium or manganese, or of aluminium with manganese, are discussed in connection with iron, chromium, and manganese. Using A and B to represent the tervalent atoms, A. Étard represented what he called **hexasulphates** by the formulæ :

$$A_2(SO_4)_6B_2 \qquad HSO_1.A_2(SO_4)_5B_2.HSO_4 \qquad (HSO_4)_2A_2(SO_4)B_2(HSO_4)_2$$

S. M. Jörgensen[2] prepared complex **cobalt polysulphates,** cobalt chloropentamminosulphatodihydrosulphate, which H. Biltz and E. Alefeld symbolize $[CoCl(NH_3)_5]_2SO_3(HSO_4)_2$. A. Benrath described $[(NH_3)_5CoCl_4]_4(SO_4)_4(H_2SO_4)_3$, or **cobalt chloropentamminodihydrosulphate,** $[Co(NH_3)_5Cl](HSO_4)_2$; and J. Meyer and co-workers, **cobalt bisdiethylenediaminosulphates,** $[Co\{C_2H_4(NH_2)_2\}_3](HSO_4)_3$; $[Co\{C_2H_4(NH_2)_2\}_3](SO_4)(HSO_3)$; $[Co\{C_2H_4(NH_2)_2\}_3]_2(SO_4)_3$; $[(NH_3)_5CoCl](HSO_4)_2$: $[(NH_3)_4Co(H_2O)(SO_4)_2]_2SO_4$; $[(NH_3)_4Co(H_2O)(SO_4)]Cl$, which are of the nature of ordinary types of amminosulphates or hydrosulphates.

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§ 34. Sulphur Heptoxide, and Persulphuric Acids

M. Berthelot[1] passed the silent electrical discharge through equal vols. of dry sulphur dioxide and oxygen, when a portion of the gas formed what he called *l'acide persulfurique* or **sulphur heptoxide,** S_2O_7, by a reaction which he symbolized : $2SO_2+2O_2=S_2O_7+O$. Sulphur trioxide and oxygen under similar conditions form the same product. In both cases, a great excess of oxygen is necessary. Conc. sulphuric acid under these conditions unites neither with oxygen nor ozone. A. Moser and N. Isgarischeff represented the reaction $SO_2+\frac{1}{2}O_2=SO_3$, and $2SO_3+\frac{1}{2}O_2=S_2O_7$. G. Bailleul also represented the heptoxide by the action of a silent discharge on a mixture of sulphur dioxide and oxygen. M. Berthelot said that sulphur heptoxide is a viscid liquid at ordinary temp., and at 0°, forms opaque, elastic, needle-like crystals, resembling those of sulphur trioxide, along with small scales and granules. Traces of water, nitric acid, nitroxylsulphonic acid, and salts from the glass vessel may retard or prevent crystallization. The heptoxide melts at 0°, and it exerts a marked vap. press. at 10°; it can be readily sublimed. The heat of formation is $(2SO_3,O)=-13{\cdot}8$ Cals.; $(2S,7O,Aq.)=126{\cdot}6$ Cals.; and $(2SO,3O)=50{\cdot}6$ Cals.

According to M. Berthelot, the sulphur heptoxide can be kept at 0° for many days without change, but after some time it slowly forms sulphur trioxide and oxygen; if warmed, the change takes place quickly; and when in contact with platinum-black, it develops oxygen, $2S_2O_7=4SO_3+O_2$. The heptoxide deliquesces in air, and forms dense fumes owing to the conversion of the vapour of the heptoxide into sulphuric acid. G. Bailleul said that the heptoxide is a mixture of equimolar proportions of sulphur trioxide and sulphur tetroxide which has an appreciable vap. press. below one mm. of mercury at temp. below 20°. It is formed only when sulphur trioxide is present in excess. By passing mixtures of sulphur dioxide and oxygen through a silent discharge tube, F. Meyer and co-workers obtained a product $SO_2.2SO_4$, and they believe that it should be possible to obtain a still higher degree of oxidation—*viz.* **sulphur tetroxide,** SO_4.

M. Berthelot said that the heptoxide dissolves in water vigorously with frothing owing to the liberation of oxygen. When a soln. of the heptoxide in dil. sulphuric acid is kept for some time, appreciable quantities of hydrogen dioxide are formed. With sulphur dioxide, dissolved in conc. sulphuric acid, it forms **sulphur pentoxide,** S_2O_5, and trioxide: $S_2O_7+2SO_2=2SO_3+S_2O_5$; with baryta-water, barium sulphate is precipitated, and some barium persulphate remains in soln. The aq. soln. of the heptoxide which escapes decomposition acts as a powerful oxidizing agent on potassium iodide, sulphurous acid, ferrous sulphate, stannous chloride, etc. M. Berthelot added that, unlike hydrogen dioxide, an aq. soln. of the heptoxide does not oxidize arsenites, oxalic acid, and chromic acid. F. Richarz, however, said that a soln. of the heptoxide in 70 per cent. sulphuric acid does oxidize oxalic acid to carbon dioxide, and any nitrogen dissolved in the liquid to nitrogen trioxide.

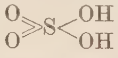
M. Traube at first thought that in the electrolysis of 40 per cent. sulphuric acid (*q.v.*), a substance corresponding with SO_4 is produced, but M. Berthelot, and subsequently H. Marshall, showed that the anhydride is really the heptoxide. M. Traube called his imaginary substance *sulphur holoxide*, on the assumption that it is sulphur trioxide in which one oxygen atom is replaced by the bivalent O_2-radicle; or, it can be regarded as hydrogen dioxide in which the two hydrogen atoms are replaced by the bivalent SO_2-radicle, *sulphuryl peroxide*, $SO_2.O_2$. As previously indicated, the alleged sulphur holoxide turned out to be a mixture of hydrogen dioxide and sulphur heptoxide. D. I. Mendeléeff regarded the heptoxide as a peroxide analogous to barium or hydrogen dioxide, and he called it *sulphuryl hyperoxide*, or *sulphur hyperoxide.*

Sulphur heptoxide can be regarded as *persulphuric anhydride* because it reacts with water, forming **persulphuric acid,** $H_2S_2O_8$: say $H_2O+S_2O_7=H_2S_2O_8$. M. Berthelot said that the same acid is formed by the action of hydrogen dioxide on sulphuric acid containing approximately $H_2SO_4+H_2O$. It is also formed when conc. sulphuric acid acts on some of the superoxides. It is, however, possible that the product is not the same persulphuric acid as that just indicated, but rather another variety which is called **permonosulphuric acid,** H_2SO_5, to distinguish it from the other acid which with the same nomenclature is called **perdisulphuric acid,** $H_2S_2O_8$. Permonosulphuric acid is also called **Caro's acid,** H_2SO_5, because N. Caro[2] first showed that the product of the electrolysis of dil. sulphuric acid which M. Traube found was different from that obtained with the conc. acid, must be due to the presence of a different chemical individual. The ratio of the contained H_2SO_4 to that of active oxygen in the case of perdisulphuric acid is 2 : 1, and in the case of permonosulphuric acid, 1 : 1. Again, while perdisulphuric acid slowly separates iodine from potassium iodide, with permonosulphuric acid, iodine is separated immediately.

It has been shown—**1**. 3, 6—that the electrolysis of very dil. sulphuric acid furnishes hydrogen and oxygen in the proportions 2 : 1 by vol. If the concentration of the acid is increased, a smaller and smaller proportion of oxygen is formed, until, with 50 per cent. sulphuric acid, in the cold, the volume of oxygen is insignificant. M. Faraday was impressed with this fact in 1834; and H. Meidinger, C. F. Schönbein, R. Bunsen, A. W. Hofmann, and A. Rundspaden observed that at the same time, the electrolyte acquired peculiar properties—*e.g.* it will oxidize antozone, and hydrogen dioxide. B. C. Brodie, however, showed that hydrogen dioxide is not formed because the liquid with chromic acid or potassium permanganate does not give the reactions characteristic of hydrogen dioxide; but since the warm liquid bleaches indigo soln., and oxidixes potassium ferrocyanide, he said that a peroxide must be present, and, by analogy with organic peroxides, he suggested that the product which is formed at the anode is peroxidized sulphuric acid, H_2SO_5. H. McLeod, and M. Berthelot confirmed these results, and the latter called the product *l'acide persulfurique* by analogy with permanganic and perchloric acid. He assigned to it the formula HSO_4; and considered it to be related to the sulphur heptoxide which he had prepared as acid and anhydride: $S_2O_7+H_2O=2HSO_4$. M. Berthelot showed that at a certain stage in the electrolysis of sulphuric acid, *l'acide persulfurique* tends to produce a combination with hydrogen dioxide which he represented by $S_2O_7.2H_2O_2$. F. Richarz thought that the hydrogen dioxide was produced by the oxidation of water by the persulphuric acid. The soln. of M. Berthelot's $S_2O_7.2H_2O_2$ slowly liberated iodine from potassium iodide, whereas the soln. containing HSO_4 liberated the iodine from potassium iodide immediately. As indicated in connection with the electrolysis of sulphuric acid, the subject became rather confused because it was not recognized that at least two definite acids can be produced—permonosulphuric acid, and perdisulphuric acid. M. Berthelot's *l'acide persulfurique* is now known to be permonosulphuric acid, H_2SO_5, and his imaginary complex, $S_2O_7.2H_2O_2$, is known to be perdisulphuric acid, $H_2S_2O_8$. The term *persulphuric acid* and *persulphate* usually apply respectively to perdisulphuric acid and the perdisulphates. The term persulphuric acid is commonly used for perdisulphuric acid, and also as a general term for all the persulphuric acids. W. C. Bray suggested calling the perdisulphates *peroxydisulphates* or simply *peroxysulphates;* and the permonosulphates, *peroxymonosulphates*—this would render it necessary to alter the naming of the peroxysulphates —**3**. 22, 23.

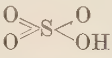
H. Marshall first supposed that the formula of perdisulphuric acid is HSO_4 because of the electrical conductivity of the potassium salt—**1**. 15, 13—and this was confirmed by J. Walker. The acid, HSO_4, was hence likened to permanganic acid, $HMnO_4$, and perchloric acid, $HClO_4$. W. Ostwald's values for the conductivity of potassium perchlorate were afterwards shown to be inaccurate, and the analogy broke down. On the other hand, R. Löwenherz showed that the factor representing the number of individuals furnished by the ionization of a molecule of the salt—**1**. 15, 10—is 2·6 when calculated from the effect of the potassium salt on the f.p., and 2·3 when calculated from the mol. conductivity. This is a closer approach to the value required for the mol. formula $K_2S_2O_8$ than to that required for KSO_4. R. Löwenherz also found that the effect of sodium perdisulphate on the f.p. of sodium sulphate is in agreement with the formula $Na_2S_2O_8$ and not with $NaSO_4$. G. Bredig obtained confirmatory evidence from the mol. conductivity, and G. Möller from the lowering of the f.p. These results are in agreement with the mol. formula $K_2S_2O_8$ for potassium perdisulphate, and with $H_2S_2O_8$ for that of the acid. These formulæ were accepted by H. Marshall in 1891. O. A. Essin calculated 10^{-6} cm. to be the distance between the charged sulphate ions which makes polymerization to persulphate possible.

J. H. Kastle and A. S. Loewenhart represented perdisulphuric acid by the formula $HO.S_2O_5.O.OH$, but the very slight acidity resulting from O.OH-radicles would probably make such an acid monobasic. P. G. Melikoff and L. Pissarjewsky represented the acid by the formula $HO.SO_2O.O.SO_2.OH$ analogous with the formulæ for the pertungstates and the permolybdates, and on the assumption that the sulphur is quadrivalent. This agrees with a hydrogen dioxide structure in which the hydrogen atoms are replaced by HSO_4''-radicles. If the electrolytic process of forming perdisulphuric acid involves the anodic discharge and union of two HSO_4''-ions, the successive stages can be symbolized (sulphur sexivalent):



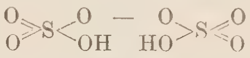
$$\begin{matrix}O\\O\end{matrix}\!>S<\!\begin{matrix}OH\\OH\end{matrix}$$

Sulphuric acid.



$$\begin{matrix}O\\O\end{matrix}\!>S<\!\begin{matrix}O\\OH\end{matrix}$$

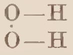
Hydrosulphate ion.



$$\begin{matrix}O\\O\end{matrix}\!>S<\!\begin{matrix}O & - & O\\OH & & HO\end{matrix}\!>S<\!\begin{matrix}O\\O\end{matrix}$$

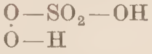
Perdisulphuric acid.

This agrees with the formation of perdisulphuric acid by the action of hydrogen dioxide on two eq. of chlorosulphonic acid, observed by J. d'Ans and W. Friederich—*vide infra*. M. Traube also regarded permonosulphuric and perdisulphuric acids as derivatives of hydrogen dioxide in which the hydrogen atoms are successively replaced by the sulphonic HSO_3-radicle:



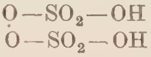
$$\begin{matrix}O-H\\O-H\end{matrix}$$

Hydrogen dioxide.



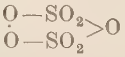
$$\begin{matrix}O-SO_2-OH\\O-H\end{matrix}$$

Caro's acid.



$$\begin{matrix}O-SO_2-OH\\O-SO_2-OH\end{matrix}$$

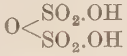
Persulphuric acid.



$$\begin{matrix}O-SO_2\\O-SO_2\end{matrix}\!>O$$

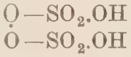
Sulphur heptoxide.

The relations of the two acids with pyro- or di-sulphuric acid will appear from the supposed graphic formulæ, based on the assumption that sulphur is sexivalent:



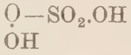
$$O<\!\begin{matrix}SO_2.OH\\SO_2.OH\end{matrix}$$

Disulphuric acid.



$$\begin{matrix}O-SO_2.OH\\O-SO_2.OH\end{matrix}$$

Perdisulphuric acid.



$$\begin{matrix}O-SO_2.OH\\OH\end{matrix}$$

Caro's acid.

T. M. Lowry and J. H. West studied the equilibrium subsisting between hydrogen dioxide and persulphuric acid in the presence of sulphuric acid and water. If the reaction be $H_2O_2+H_2SO_4\rightleftharpoons H_2SO_5+H_2O$, the equilibrium condition from the law of mass action is $C_1C_4=K_1C_2C_3$, where C_1, C_2, C_3, and C_4 represent the concentrations of the four components of the system; similarly, if the reaction be $H_2O_2+2H_2SO_4\rightleftharpoons H_2S_2O_8+2H_2O$, $C_1C_4{}^2=K_2C_2C_3{}^2$; and if $H_2O_2+4H_2SO_4\rightleftharpoons H_2S_4O_{14}+4H_2O$, $C_1C_4{}^4=K_4C_2C_3{}^4$. The corresponding values are:

$$\frac{C_1}{C_2}=\frac{3}{2}\frac{C_3}{C_4} \qquad \frac{C_1}{C_2}=3\left(\frac{C_3}{C_4}\right)^2 \qquad \frac{C_1}{C_2}=12\cdot6\left(\frac{C_3}{C_4}\right)^4$$

respectively. The corresponding curves are plotted in Fig. 102. The curves corresponding with the equations for K_1 and K_2 do not fit the observed data, whereas the results fit the curve for K_4 very well. The slight deviations are attributed to the simultaneous formation of perdisulphuric acid, so that the equilibrium condition assumes the form $C_1/C_2=K_2(C_3/C_4)^2+K_4(C_3/C_4)^4$, where the constants $K_2=0\cdot63$, and $K_4=10\cdot96$. These important conclusions have not been accepted, presumably because of the two objections: (i) The hydrogen dioxide was estimated by titration with permanganate, a process which was subsequently shown to be untrustworthy under these conditions of the experiments; and (ii) although equilibrium was obtained in conc. soln., the liquids were diluted before the titrations were made, thus introducing another equilibrium condition. H. Ahrle found no evidence of per-

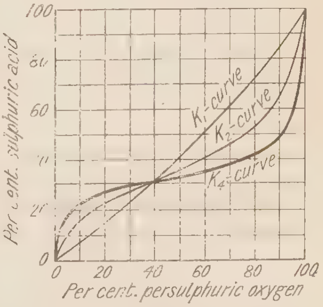


FIG. 102.—Relations between the Concentrations of Sulphuric Acid and the Persulphuric Acids.

tetrasulphuric acid in dil. soln. H. Palme assumed that the hydrolysis of perdisulphuric acid proceeds *viâ* the consecutive reactions: $H_2S_2O_8+H_2O=H_2SO_5+H_2SO_4$, with the velocity constant k_1, followed by $H_2SO_5+H_2O=H_2O_2+H_2SO_4$, with the constant k_3. Both reactions are unimolecular and irreversible. With increasing conc. of sulphuric acid, both velocity constants increased at a rate greater than the acid conc., but the ratio k_1/k_3 remained constant, 39·8. No relation between the hydrogen-ion conc. and the velocity of reaction could be discovered, and the conclusion of M. G. Levi and E. Migliorini, that the undissociated persulphuric acid, the presence of which would be favoured by increasing hydrogen-ion conc., is less stable than its salts, was not confirmed. The experiments were not carried far beyond the time after which oxygen begins to be evolved, through the reaction $H_2S_2O_8+H_2O_2=2H_2SO_4+O_2$. This makes Caro's acid a monosulphonic acid derivative of hydrogen dioxide. T. M. Lowry has discussed the electronic structure—*vide supra*, hyposulphurous acid.

A. von Bäyer and V. Villiger showed that permonosulphonic acid has a 1 : 1 mol. ratio for sulphuric acid and active oxygen, $H_2SO_4 : O$, and that this agrees with the ratio required for M. Traube's sulphuryl holoxide. T. S. Price showed that the action of the acid on potassium iodide is in agreement with A. von Bäyer and V. Villiger's observations. A. Bach showed that although Caro's acid when diluted does not reduce potassium permanganate, yet, undiluted, it rapidly decolorizes a soln. of the latter in conc. sulphuric acid; the titration is sharply defined, and the whole of the oxygen of the persulphate is evolved together with that due to the permanganate. The view that a catalytic decomposition of the Caro's acid here occurs, is excluded by the fact that the latter yields no oxygen either with manganous sulphate or with the liquid obtained after titrating Caro's acid with permanganic anhydride. The existence in Caro's reagent of a "higher persulphuric acid," $(SO_3H.O.O.SO_3H)_3$, is therefore assumed, which on dilution yields the acid, $SO_3H.O.OH$, incapable of reducing potassium permanganate. In the higher acid an ozonoid grouping is probable, since Caro's acid is formed on dissolving sodium dioxide in well-cooled sulphuric acid, although, on warming, as shown by E. Bamberger, ozone is evolved. H. E. Armstrong and co-workers suggested that the progressive dilution of the assumed pertetrasulphuric acid furnishes, by hydrolysis, a series of persulphuric acid which they called

$$\begin{array}{l} HO.SO_2.O.SO_2.\underset{\cdot}{O} \\ HO.SO_2.O.SO_2.O \end{array}$$

Pertetrasulphuric acid, $H_2O_2.4SO_3$.

$$\begin{array}{l} HO.SO_2.\underset{\cdot}{O} \\ HO.SO_2.O \end{array}$$

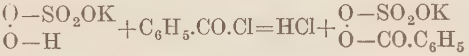
Perdisulphuric acid, $H_2O_2.2SO_3$.

$$\left.\begin{array}{l} HO.O.SO_2 \\ HO.O.SO_2 \end{array}\right> O$$

Peranhydrosulphuric acid, $(HSO_4)_2O$.

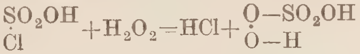
H. E. Armstrong and T. M. Lowry suggested that Caro's acid has the formula $H_2O_3.2SO_3$ or $H_2S_2O_9$. They said that when Caro's acid is heated, it becomes acid, and the ratio of the increase in acidity to the loss of active oxygen $SO_3 : O=1 : 2$, a result not in harmony with the formula H_2SO_5, because the salt of such an acid should remain neutral after the removal of the peroxidic oxygen: $2CaSO_5=2CaSO_4+O_2$. On the other hand, if the formula be $H_2S_2O_9$, the facts are explained: $CaS_2O_9+H_2O=CaSO_4+H_2SO_4+O_2$. The anhydro-acid is assumed to be derived from the permonosulphuric acid: $2HO.SO_2.O.OH=H_2O+(HO.O.SO_2)_2O$. T. S. Price showed that if the hydrolysis occurs according to the equation: $H_2S_2O_8+H_2O=H_2SO_5+H_2SO_4$, every mol. of the permonosulphuric acid which is formed will increase the total acidity by an eq. amount of sulphuric acid. The ratio of the iodine value to the increase of H_2SO_4 acidity should be 2·59 if H_2SO_4 is dibasic, and 5·18, if monobasic. With sodium hydroxide, the results agree with the assumption that the product is monobasic H_2SO_4—with barium hydroxide, the acid is decomposed. The results did not agree with the assumption that the degradation of the perdisulphuric acid proceeds $2H_2S_2O_8=H_2S_4O_{14}+H_2O_2$. According to M. Mugdan, either formula—$H_2S_2O_9$ or H_2SO_5—accounts for the reaction with potassium iodide; in the one case, the reaction is $H_2S_2O_9+4KI=2K_2SO_4+2I_2+H_2O$, and in the other case $H_2SO_5+2KI=K_2SO_4+I_2+H_2O$.

This does not decide whether Caro's acid is monobasic, H_2SO_5, or dibasic, $H_2S_2O_9$. The analysis of the potassium salt is not conclusive, since $KHSO_5$ would have the same ultimate composition as the salt $K_2S_2O_9.H_2O$; but T. S. Price showed that the analysis agrees with the formula $KHSO_5$, and not with $K_2S_2O_9$. This agrees with the hypothesis that Caro's acid is monobasic permonosulphuric acid, H_2SO_5, and that the potassium salt is $KHSO_5$. R. Willstätter and E. Hauenstein found that benzoyl chloride, $C_6H_5.CO.Cl$, reacts with the potassium salt of Caro's acid, forming the benzoyl derivative. This reaction corresponds with the monobasicity of the acid:



$$\begin{matrix}O-SO_2OK\\ O-H\end{matrix}+C_6H_5.CO.Cl=HCl+\begin{matrix}O-SO_2OK\\ \vdots\\ O-CO.C_6H_5\end{matrix}$$

It is very unlikely that this result would occur if the formula of the salt in question were $K_2S_2O_9.H_2O$. J. d'Ans and W. Friederich prepared an aniline salt as a white precipitate in ethereal soln. The composition agreed with $C_6H_5.NH_3.HSO_5$. J. d'Ans and W. Friederich's synthesis of Caro's acid by the action of the calculated quantity of chlorosulphonic acid, $SO_2Cl(OH)$, on pure hydrogen dioxide in the cold:



$$\begin{matrix}SO_2OH\\ Cl\end{matrix}+H_2O_2=HCl+\begin{matrix}O-SO_2OH\\ \vdots\\ O-H\end{matrix}$$

is in agreement with the view of the molecular formula H_2SO_5. Another mol. of chlorosulphonic acid converts the permonosulphuric acid into perdisulphuric acid. Fluosulphonic acid can be used in place of chlorosulphonic acid. E. Weitz found that the ammonium salts of monobasic acids are more soluble in the presence of ammonia than in water, while with the salts of polybasic acids, the solubility is diminished; by this test, persulphuric acid is monobasic or rather "doubly monobasic" $(HSO_4)_2$, since there are two separate nuclei in the molecule each containing an acid-hydrogen atom.

The preparation of perdisulphuric acid and the perdisulphates.—F. Fichter and W. Bladergroen noticed that persulphates are formed when fluorine acts on hydrosulphates. J. d'Ans and W. Friederich prepared anhydrous perdisulphuric acid by gradually adding a mol of anhydrous hydrogen dioxide to two mols of chlorosulphonic acid (or fluosulphonic acid): $2ClHSO_3+H_2O_2=H_2S_2O_8+2HCl$. The hydrogen chloride is sucked from the crystals at the pump, and the mother-liquor is separated by the centrifuge. The soln. obtained by mixing hydrogen dioxide with sulphuric acid, formerly thought to be this acid, is now regarded as the permonosulphuric acid. F. Fichter and K. Humpert observed that presumably perdisulphates are formed when fluorine acts on a cold sat. soln. of ammonium or potassium hydrosulphate or sulphate: $3K_2SO_4+F_2+2HF=K_2S_2O_8+3KF+KFSO_3+H_2O$; and F. Fichter and W. Bladergroen observed that this product is formed in greatest amount with well-cooled $2{\cdot}35M\text{-}H_2SO_4$, and from soln. of sulphates or hydrosulphates with the eq. of 4·4 per cent. SO_4. The substance oxidizes manganous sulphate rapidly to permanganate, precipitates silver peroxide immediately from silver nitrate soln., and also oxidizes phenolphthalein to fluorescein and other hydroxylated derivatives. The substance originally obtained by M. Berthelot on subjecting a mixture of sulphur dioxide and oxygen to the discharge in an ozonizer, also gives these reactions when dissolved in sulphuric acid, and it is concluded that the peroxide produced by fluorine is probably a sulphur tetroxide (SO_4 or S_2O_8) identical with that present in M. Berthelot's substance. The work of P. Schoop, G. Darrieus and P. Schoop, H. E. Armstrong and G. E. Robertson, K. Elbs and O. Schönherr, etc.—*7*. 47, 4—has shown that this acid is formed about the positive electrode during the charging of the lead accumulator (*q.v.*). M. Berthelot observed that in preparing the sulphuric acid soln. of persulphuric acid it is better to use a small platinum wire anode than an anode with a larger surface so as to minimize the possible decomposition of the persulphuric acid, by contact with the platinum; and H. Marshall found that a large anode, involving a low current density is very unfavourable to the production of perdisulphuric acid.

M. Berthelot considered that the formation of perdisulphuric acid is a process of oxidation by the hydrogen dioxide formed during the electrolysis : $2H_2SO_4+H_2O_2=H_2S_2O_8+2H_2O$. It is true, as indicated above, that K. Elbs and O. Schönherr, E. Müller and H. Schellhaass, etc., were unable to verify M. Berthelot's statement that hydrogen dioxide is formed in the operation, but their experiments lasted only a few hours, whereas M. Berthelot continued the electrolysis for days. As shown by K. Elbs and O. Schönherr, it is probable, however, that during the prolonged electrolysis the perdisulphuric acid is broken down into permonosulphuric acid, and then into hydrogen dioxide ; and this explains how the properties of the soln. vary with their concentration, and age. M. Traube suggested that an atom of nascent oxygen unites with an atom of oxygen in the sulphuric acid, forming the complex represented in the equation : $2H_2SO_4+O=S_2O_6(O_2)H_2+H_2O$. The general opinion is that persulphate is not due to a process of oxidation, but rather by the union of two HSO_4-ions at the moment of discharge or by the condensation of sulphuric acid with the loss of hydrogen. Hence, said H. Marshall, the formation of persulphate from sulphate by electrolysis is similar to the formation of tetrathionate from thiosulphate by the action of iodine. The tetrathionates, $(MSO_3)_2S_2$, may thus be compared with the persulphates, $(MSO_3)_2O_2$, and the anhydrosulphates, $(MSO_3)_2O$, with the trithionates, $(MSO_3)_2S$. If persulphuric acid be formed during the discharge of the HSO_4-ions conveying the current in soln. of sulphuric acid of the concentration employed, there is a greater opportunity for the formation of persulphuric acid where the HSO_4-ions are closely packed together at the moment of discharge—that is, when a high current density at the anode is employed. W. Starck found that the formation of persulphuric acid runs parallel with the presence of HSO_4-ions up to a certain concentration (40 per cent. acid). The poorer yield of persulphuric acid from this point onwards is probably due to its instability in conc. sulphuric acid soln., rather than to a decrease in the quantity of HSO_4-ions. H. Marshall accordingly stated that the conditions favouring good yields are (i) an anode soln. containing the highest possible concentration of HSO_4'-ions—not SO_4''-ions ; (ii) a high current density ; and (iii) a low temp.—because persulphuric acid readily decomposes when warmed.

M. Berthelot examined the effect of the *concentration* of the sulphuric acid on the yield of persulphate, and F. Richarz found that the maximum yield was obtained with 40 per cent. sulphuric acid with a high current density at the anode. K. Elbs and O. Schönherr found that the yields of persulphate with sulphuric acid of sp. gr. *S* and a current density of D amp. per sq. dm. were :

S	1·15	1·20	1·35	1·45	1·50	1·55	1·60	1·65	1·70
D 5	—	—	3·9	32·9	52·0	59·6	60·1	55·8	40·0
50	—	4·4	60·5	73·1	74·5	66·7	63·8	52·0	—
100	7·0	20·9	71·3	75·7	78·4	71·8	65·3	50·8	—

The decreased yield with acid of sp. gr. 1·50 was attributed to the persulphuric acid itself taking part in the conduction of the current and being so destroyed ; it may also be due to the rapid conversion of perdisulphuric to permonosulphuric acid by sulphuric acid of this concentration, and the subsequent decomposition of the permonosulphuric acid. The more dil. the acid, the later is the period at which the maximum yield is obtained. The Oesterreichische Chemische Werke recommended electrolyzing a soln. containing 500 grms. of conc. sulphuric acid per litre, at 20° by a current of 400 amp. per litre. The yield was over 70 per cent. E. Müller and H. Schellhaass obtained a maximum yield with an acid of sp. gr. 1·39 and their results at 6° to 16° with an acid of this conc., and a current density of 75 amps. are :

Time	15	30	60	120	180	240	360	420 mm.
Volts	5·8	5·8	5·8	5·9	6·1	6·1	6·1	6·2
H_2SO_5	—	0·09	0·40	1·38	2·70	4·40	7·45	10·52
$H_2S_2O_8$	—	1·91	3·52	—	8·72	9·40	13·52	10·93
H_2O_2	—	—	—	—	—	—	trace	trace
Efficiency	65·47	—	68·83	60·98	50·15	36·60	17·51	—0·70 per cent.

The results are plotted in Fig. 103. With a current density of 25 amps. at 12°-13°, the numbers were less. At first, the increase in the conc. of the persulphuric acid runs parallel with the decrease in the current efficiency; but later, the conc. of the persulphuric acid becomes almost constant while the current efficiency decreases. The permonosulphuric acid is responsible for the time-yield curve. J. Salauze, O. A. Essin, and O. A. Essin and E. Krylow examined the electrolytic process.

W. Moldenhauer found that the higher the anodic potential, the greater the formation of perdisulphuric acid. It is suggested that the initial increase in current efficiency is due to a rise in the anodic potential, while the subsequent fall is accompanied by a steady decrease in the proportion of permonosulphuric acid present in the soln. The acid, which is formed from the perdisulphuric acid, is destroyed at the anode: $H_2SO_5+2OH'=H_2SO_4+O_2+H_2O$. The quantities of permonosulphuric acid formed and decomposed in unit time increase with the conc. of persulphuric acid. The permonosulphuric acid acts as a depolarizer, and prevents an increase in the anodic potential, thus diminishing the yield of perdisulphuric acid. K. Elbs and O. Schönherr found that an increased yield occurs with an increase in *current density*, *D* amp. per sq. dm., thus, with sulphuric acid of sp. gr. 1·35, in 50 minutes at 8° to 10°:

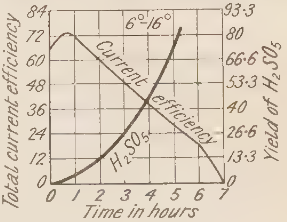


Fig. 103.—The Time-yield of Permonosulphate and Current Efficiency in the Electrolysis of Sulphuric Acid of sp. gr. 1·39.

D	4	28	100	500
Yield	0·7	55·3	61·2	67·5 per cent.

These results have been confirmed by E. Müller and H. Schellhaass, and others. A rise in *temperature* lessens the yields, and at 60° the yield is practically zero, for the perdisulphuric acid decomposes as fast as it is formed. W. Starck said that the formation of persulphuric acid is favoured by a fall of temp. in agreement with the probable increase of HSO_4-ions as the temp. falls. W. Moldenhauer found that the cooling of the anode increases the yield. F. Richarz, K. Elbs and O. Schönherr, and G. I. Petrenko found that the yield is dependent on the *nature of the electrodes*. The efficiency of the platinum anode gradually diminishes as the electrolysis proceeds, and at the same time the surface is roughened. This may be due to the oxidation of the platinum, which then acts catalytically on the decomposition of the persulphuric acid. The efficiency was found by F. Richarz to be restored by heating the anode to redness. K. Elbs and O. Schönherr made a similar observation, and added that a freshly-prepared platinized electrode gives poor results, but becomes efficient after heating to redness when the surface acquires a metallic lustre. G. I. Petrenko said that iridium electrodes give smaller yields than platinum anodes, and they dissolve more readily in the anode liquor. According to the Farbenfabriken vorm. F. Bayer, the electrolytic preparation of the persulphates can be carried out without the addition of electrolytes or the use of a diaphragm if tin or aluminium electrodes are used. O. A. Essin studied the effect of the conc. of sulphate and persulphate in the electrolyte on the current efficiency.

K. Elbs and O. Schönherr found that the presence of some *foreign substances*—*e.g.* the sulphates of ammonium, potassium, aluminium, and nickel—favours the formation of persulphuric acid; the sulphates of sodium, copper, magnesium, zinc, and chromium have no marked effect. A drop of conc. hydrochloric acid increased the yield from 45·9 to 69 per cent. E. Müller and H. Schellhaass attributed the effect to (i) the raising of the anodic potential; and (ii) to the chemical destruction of permonosulphuric acid, thus preventing its depolarizing action. The presence of hydrofluoric acid raised the anodic potential and increased the current efficiency; hydrochloric acid raises the anodic potential and destroys chemically the permonosulphuric acid; sulphurous acid has a good effect because it destroys chemically the permonosulphuric acid; and with the sulphates indicated above, the anodic potential is sometimes raised, and sometimes lowered, and the current efficiency varies in a corresponding way. A. Mazzucchelli found that the yields were much improved by adding a small proportion of perchloric acid, or of ammonium or potassium perchlorate. No hydrochloric acid was formed; and A. Mazzucchelli and B. Romani attributed the effect to an increase in the anodic overvoltage. J. Salauze tested the efficiency of different methods of making ammonium persulphate. With chromate as accelerator in neutral soln., the chromium hydroxide which forms on the platinum cathode is very fragile, and is dissolved if the soln. becomes slightly acid. The yield is as good at 8° as it is at 22°, and the yield is improved if traces of chlorides are present. Owing to the great solubility of ammonium persulphate in neutral or alkaline soln., prolonged electrolysis is needed before the salt separates. The ammonium persulphate separates readily in acidic soln., and the process does not require so much attention with acidic soln. A little potassium ferrocyanide as accelerator slightly improves the yield, but the product is contaminated with a little prussian blue, which is difficult to remove. The conditions for a 70–75 per cent. yield are: (i) a low temp.; (ii) a conc. soln. of sulphuric acid corresponding with the presence of ammonium hydrosulphate; (iii) a fresh platinum anode eq. to a current density of amps. per sq. dm.; (iv) a platinum cathode with the largest possible current density; and (v) the presence of a trace of chlorides.

K. Elbs and O. Schönherr prepared perdisulphuric acid by the electrolysis of sulphuric acid of sp. gr. 1·35 to 1·50, with or without the addition of ammonium sulphate. The apparatus employed consisted of a divided cell formed by a porous jar of 100 c.c. capacity, standing in a beaker. A cylinder of lead or platinum of 150 sq. cm. surface, surrounding the jar, formed the cathode. The anode was a platinum wire or foil dipping into the jar. The cell was surrounded with ice. Sometimes the arrangement was reversed, a ring of platinum wire in the outer cell forming the anode, and a coil of lead pipe in the jar acting both as cathode and as a cooling worm. The resulting anolyte after being electrolyzed overnight—current, 2 amp.; current density, 500 amp. per sq. dm.; and 4 volts—contained 510 grms. of persulphuric acid, and 129 grms. of sulphuric acid per litre—no hydrogen dioxide was present. It was treated at 0° with the quantity of barium carbonate necessary to precipitate the sulphuric acid—barium persulphate is fairly soluble in water—and filtered. The filtrate contained neither barium nor sulphuric acid. M. Traube said that the barium carbonate also decomposes any permonosulphuric acid—he called it sulphuryl holoxide—which might have been present, forming hydrogen dioxide and oxygen. M. Berthelot used barium hydroxide in place of the carbonate; and M. Traube, barium phosphate. A. von Bäyer and V. Villiger obtained perdisulphuric acid by treating a dil. soln. of the barium salt with the calculated quantity of dil. sulphuric acid.

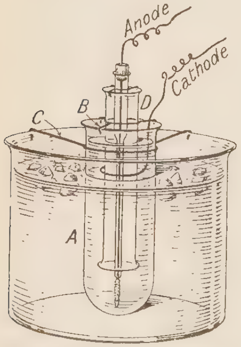


Fig. 104.—The Preparation of Potassium Perdisulphate.

The preparation of small quantities of potassium persulphate by the electrolysis of a sat. soln. of potassium sulphate in sulphuric acid of sp. gr. 1·2 to 1·3, is thus described by K. Elbs:

> The soln. is placed in a test-tube, *A*, Fig. 104, so that the test-tube is about three-fourths filled. The test-tube is fixed in a large beaker by means of the wire *C*. A glass cylinder, *D*, is fixed in the test-tube by means of the wire *B*. A coil of platinum wire—the cathode—is allowed to dip into the solution of potassium sulphate as indicated in the diagram; and a platinum wire sealed to a piece of glass tube so that about $1\frac{1}{2}$ to 2 cms. of the wire from the tube forms the anode. This is fixed within the cylinder. The large beaker is filled with water in which pieces of ice are floating—"iced-water." A current of about one or two ampères is sent through the soln.

—the current density at the anode is about 100 amps. per sq. cm. Hydrogen appears at the cathode; and a white crystalline mass accumulates at the anode. In about 45 minutes the current may be stopped, and the white crystals of potassium persulphate collected on a filter paper. The salt is washed first with alcohol and finally with ether.

K. Elbs recommended the following process for ammonium persulphate :

The bath consists of a porous pot of 80 to 150 c.c. capacity standing in a beaker. The anode liquid is a cold sat. soln. of ammonium sulphate. The anode liquid is kept approximately saturated with ammonium sulphate by suspending in the anode compartment a small test-tube pierced with a number of small holes, and filled with the salt. The cathode liquid is a mixture of sulphuric acid with one or two vols. of water. The cathode is a lead tube coiled spirally round the porous pot, and cold water or iced water is run in a continuous stream through the tube so as to keep the temp. of the anode compartment between 10° and 20°. The anode consists of a spiral of platinum wire of 1 to 2 sq. cms. surface area; it dips about half-way down in the liquid contained in the porous pot. The current employed is 5 to 10 amps. giving an anode current density of 500–1000 amps. per sq. dm. During the electrolysis, a current of highly ozonized oxygen is slowly evolved at the anode. From time to time, after intervals of three or four hours, the electrolysis is stopped, and the contents of the porous pot filtered through glass wool; the crystals thus separated are dried on a porous plate, whilst the filtrate is shaken with crystallized ammonium sulphate and thus again saturated, after which it is poured back into the porous pot. The liquid in the cathode portion of the cell becomes neutralized as a result of the migration of sulphuric acid anions away from it and that of ammonium-ions into it, and before it becomes alkaline must be syphoned off and replaced by fresh sulphuric acid. On the other hand, the anode liquid becomes poorer in ammonia and more concentrated in sulphuric acid, on account of the migration of the ammonium ion out of it and that of the sulphuric acid anion into it; this alteration is not compensated for by the separation of ammonium persulphate and the occasional saturation of the soln. with ammonium sulphate; it is consequently necessary about every two operations to add to the anode liquid by means of a funnel with a capillary tube, with cooling, a quantity of ammonia, saturated with ammonium sulphate, sufficient nearly to neutralize the free acid. The precipitate which is thus formed consists of ammonium persulphate, and is poured with the liquid into the porous pot. At the first operation the separation in the porous pot is rather small, at the later ones considerable, since it is necessary for the liquid to become saturated with ammonium persulphate before a separation of the solid salt can commence; in the later operations this is the case at the start. When the experiment is finished, the anode liquid is either preserved for later experiments, or the persulphate contained in it is recovered in the form of a crystalline precipitate of potassium persulphate by careful addition of a moderately conc. soln. of potassium carbonate. It is very important before each experiment to wash the anode with water and heat it to glowing. The current efficiency exceeds 70 per cent., the yield of material 60 per cent. The raw product contains as chief impurity about 5 per cent. of ammonium sulphate; the salt can be obtained crystallized in a pure and fine condition, although necessarily with considerable loss, if water at 50° is quickly saturated with the salt and then allowed to cool slowly to a low temp. Ammonium persulphate can be preserved from decomposition only in completely dry condition. For the quantitative determination, the soln. of persulphate is poured into an excess of strongly acid ferrous ammonium sulphate, and the excess of ferrous salt titrated back with permanganate. It must be observed, however, that, in the cold, Mohr's salt is not momentarily oxidized by the persulphates, but that the reaction takes several minutes, as indicated by M. le Blanc. In the preparation of persulphates, hydrogen dioxide and its derivatives are also formed in the anode chamber; these can be determined directly by means of permanganate. In order, therefore, to follow the course of the electrolysis, samples of the anode liquid are titrated first with permanganate, then reduced with ferrous ammonium sulphate and titrated back with permanganate; in this way the first determination gives the content of hydrogen dioxide, and the second that of persulphate. With the apparatus described above and under the same conditions, potassium persulphate can also be prepared. In consequence of the difficult solubility of potassium sulphate the method is not very satisfactory; but, on account of the still smaller solubility of potassium persulphate, it is simple and effective.

According to W. Moldenhauer, in the electrolysis of sulphuric acid of sp. gr. 1·45 or less, the yield of persulphuric acid is improved by cooling the anode to −2°, whilst with more conc. acids it is diminished; these results seem to depend on the conc. of the HSO_4-ions present. In the preparation of ammonium persulphate a small improvement in yield is obtained by cooling the anode to −2°. In the prolonged electrolysis of sulphuric acid, E. Müller and R. Emslander found that the final concentration of perdisulphuric acid is greater, the greater the current density, but the final conc. of permonosulphuric acid is independent of current density. The total conc.—perdisulphuric and permonosulphuric acids—increases to a maximum in the course of the electrolysis ; but whilst the conc. of permonosulphuric acid increases continuously up to a stationary state, that of perdisulphuric acid attains a maximum, and then falls to a constant value. E. Müller and O. Friedberger examined the effect of various electrolytes, and of additions to the electrolytes used in the preparation of ammonium or potassium persulphate. They employed an individual cell with a current density of 48 amps. per sq. dm., at 7° to 8°. A sat. soln. of potassium sulphate is not a satisfactory electrolyte since the yield of potassium persulphate is small—15·2 per cent. after 1½ hrs.—and the electrolyte gradually becomes alkaline, and when the alkalinity has reached a certain stage, the formation of persulphate ceases. The presence of potassium chromate does not affect the yield. A sat. soln. of potassium hydrosulphate gives a 35 per cent. yield, and the yield is not affected by additions of chromate. With an acid soln. of ammonium sulphate—when 1 c.c. is eq. to 1·6 c.c. *N*-KOH—a 75 per cent. yield of ammonium persulphate was obtained the first half hour ; afterwards the yield decreased because of cathodic reduction. After 7 hrs.' electrolysis, when the acidity of the soln. had diminished very much, the addition of chromate decreased the cathode reduction and increased the yield to 83 per cent. An 80 per cent. yield is obtained with a neutral soln. of ammonium sulphate, to which sulphuric acid is added from time to time to neutralize the free ammonia, and to which chromate has been added. The voltage required without a diaphragm was 5·9 compared with the 8 volts needed when a diaphragm was used.

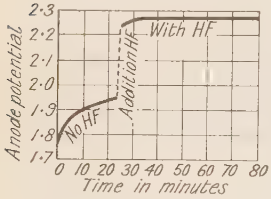


Fig. 105.—Effect of Hydrofluoric Acid on the Anodic Potential of Sulphuric Acid.

M. G. Levi found that in preparing ammonium persulphate a low temp. is necessary. The yield in a cell with a current density of 25 amp. per sq. dm. began to diminish from 60·8 per cent. at 30° to 53·7 per cent. at 40° and 40·0 per cent. at 50°, when the yield at 10° was 60·0 per cent. This is due to the fact that the ammonium persulphate begins to decompose only at 40°. In studying the effect of different electrodes with an electrolyte containing some chromate, it was found that with a platinum anode having a current density of 26 amps. per sq. dm., and a current density of 15 amps. per sq. dm. at the cathode, the yield with a platinum cathode, up to 35°, was 64 per cent. ; with a nickel cathode, 63 per cent. ; with a lead cathode, 54·4 per cent. ; and with a carbon cathode, 65·9 per cent. An anodic current density varying from 6 to 50 amps. per sq. dm. had very little influence on the yield. The Konsortium für elektrochemische Industrie observed that the deposition of chromic oxide on the cathode is uncertain, and, at 10°–20°, the deposit consists of chromium metal which is no use as a diaphragm. E. Müller observed that with an anodic current density of 20 amps. per sq. dm., the addition of 20 vols. per cent. of hydrofluoric acid to a soln. of potassium hydrosulphate increased the yield of persulphate from 50 to 80 per cent. ; and in the case of sodium hydrosulphate, from 1 to 28 per cent. The anodic potential, measured against a 0·1*N*-calomel electrode, with a current density of 0·5 amp. per sq. dm. rose as indicated by the curve, Fig. 105, when hydrofluoric acid was added. The addition of sulphuric acid produced no rise of potential so that the increase with hydrofluoric acid must be due to that acid or the fluoride-ions, and not to the increase in the $H^{\cdot}$-ions, or the acidity of the soln. It is supposed that in acidic soln., the permonosulphuric acid formed by the hydrolysis of the perdisulphuric acid, acts as a depolarizer ; and the higher the anodic potential, the more readily will the permonosulphuric acid be destroyed : $H_2SO_5+2OH'=H_2SO_4+O_2+H_2O$, and the greater the yield of persulphate. O. A. Essin observed that the current yield in preparing ammonium persulphate is independent of the current density between 1 and 16 amps. per sq. cm. ; and, as found by M. G. Levi, it is independent of the temp. between 10° and 30° provided that the soln. is kept sat. with sulphate. Within the above ranges of anodic current densities and temp., the current yield is given by $100C_1/(C_1-C_2)$ per cent., where C_1 and C_2 respectively denote the conc. of sulphate and persulphate.

According to E. Müller and H. Schellhaass, in a prolonged electrolysis, the quantity of permonosulphuric acid keeps on increasing until the stage is reached where the rate of formation of perdisulphuric acid at the anode is equal to the rate at which it changes to permonosulphuric acid. The current yield of perdisulphate is then zero. The destruction of the permonosulphuric acid is of use only in certain cases. If the $S_2O''_8$-ions remain in soln., meaning that solid persulphate is not precipitated, and the stage is reached when perdisulphuric acid changes into permonosulphuric acid, the destruction of the latter, as fast as it is formed, will not increase the current yield of the former. On the other hand, if solid persulphate is precipitated before the soln. has attained that concentration when its rate of formation is equal to the velocity of formation of perdisulphuric acid, the maximum rate of formation of the permonosulphuric acid is less than the rate of formation of perdisulphuric acid, and the difference in the two velocities is all the greater, the less the solubility of the perdisulphate. In this case, the permonosulphuric acid can be advantageously destroyed by sulphurous acid. The speed of the conversion of the perdisulphuric acid to permonosulphuric acid increases with increasing acidity of the soln., and in slightly acid soln. of ammonium perdisulphate, the rate of conversion is so small that even in sat. soln. it does not attain the limiting concentration where the rate of its degradation never becomes equal to its rate of formation. Hence, ammonium perdisulphate is readily formed in weakly acid soln. On the other hand, with sodium and potassium persulphates strongly acid soln. are needed to obtain the necessary conc. of HSO_4'-ions. The low solubilities of potassium and sodium persulphates in strongly acid soln. favour the formation of these salts; but the solubilities are still great enough to lead to the formation of so much permonosulphuric acid that to maintain a high current efficiency, it is advisable to add the destroyer—sulphurous acid. H. Erlenmeyer studied the effect of nitrogen, under press., on the electrotype process.

The formation of persulphuric acid by the action of fluorine on sulphuric acid was discussed by F. Fichter and K. Humpert, F. Fisher and K. Massenez, and W. Bladergroen.

The properties of perdisulphuric acid and perdisulphates.—J. d'Ans and W. Friederich[3] found that the crystals of anhydrous perdisulphuric acid melt with a slight decomposition at about 65°. They can be kept for months at ordinary temp., but oxygen is slowly evolved. The crystals are hygroscopic. They are hydrolyzed when dissolved directly in water, forming sulphuric and permonosulphuric acids, but this hydrolysis can be prevented by first dissolving the acid in ether, and gradually adding the ethereal soln. to cold water. The potassium salt can be prepared from this soln. by neutralization with potassium carbonate or hydroxide. When the ethereal soln. is cooled by solid carbon dioxide, a white complex salt, $H_2S_2O_8.2(C_2H_5)_2O$, is formed. Anhydrous persulphuric acid vigorously attacks most organic substances; solid paraffin is gradually changed; and explosions may be produced with aniline, benzene, nitrobenzene, phenol, alcohol, ether, etc., unless care be taken in the mixing.

The properties of the sulphuric acid soln. of persulphuric acid, as described in the early literature, are to some extent confused because it was supposed that only the perdisulphuric acid was present, whereas both or either may have been under observation. K. Elbs and O. Schönherr found the **specific gravity** of persulphuric acid and of sulphuric acid to be at 14°/4°:

Sp. gr.	.	1·042	1·096	1·154	1·246
$H_2S_2O_8$	.	7·2	15·4	23·6	35·2 per cent. by weight
H_2SO_4	.	6·2	13·8	21·4	33·11 ,, ,,

so that soln. of persulphuric acid are specifically lighter than soln. of sulphuric acid containing an eq. proportion of acid. According to the Oesterreichische Chemische Werke, persulphuric acid can be distilled by heating its soln. directly under reduced press. by an alternating current below one ampère per sq. cm. The number of alternations can be as low as 50 with carbon electrodes, but more are required with platinum electrodes. M. Berthelot gave for the **heat of formation** from rhombic sulphur $(2S,8O,H_2,Aq.)=316·2$ Cals., and $(2S,7O,H_2O,Aq.)=247·2$ Cals. Persulphuric acid, being an endothermic compound, requires an extraneous source of energy for its formation. Its heat of decomposition is: $H_2S_2O_8.nH_2O+H_2SO_4=3H_2SO_4.nH_2O+O+34·8$ Cals.; and $S_2O_{7aq.}+2H_2O_{aq.}=2H_2SO_{4aq.}+O+13·8$ Cals. According to H. Giran, $(S_2O_{7solid},Aq.)=56·71$ Cals. J. L. R. Morgan and R. H. Crist found the extinction coeff., k, in the usual relation $I=I_0e^{-kd}$, or $k=\{\log(I_0/I)\}/d$, when d denotes the depth of the cell=2 cms. The results are summarized in Fig. 106. D. Vitali found that aq. soln. of not quite pure persulphates show a bluish-violet **fluorescence.** R. Glocker and O. Risse studied the decomposition of an aq. soln. exposed to X-rays. According to F. Richarz, the **polarization** which occurs in the electrolysis of dil. sulphuric acid is due to the formation of persulphuric acid, ozone, and hydrogen dioxide, and it gives rise to an e.m.f. The e.m.f. necessary to overcome polarization in the electrolytic cell is eq. to $Pt \mid H_2SO_{4aq.},H_2S_2O_{8aq.} \mid Pt=0·61$ Daniell's units; and the heat developed in the reaction: $H_2S_2O_{8aq.}=2H_2SO_{4aq.}+O+0·56$ Daniell's units. The agreement between the calculated and observed values in this reaction agrees with the assumption that persulphuric acid is produced as a primary electrolytic process, and this is confirmed by the high e.m.f. of the element $Zn \mid H_2SO_{4aq.},H_2S_2O_{8aq.} \mid Pt=2·06$ Daniell's units. According to R. Peters, a persulphate in sulphuric acid soln. is an energetic depolarizer, and it can be advantageously used in place of nitric acid in Bunsen's cell. F. Weigert studied the electrolytic reduction of soln. of potassium persulphate.

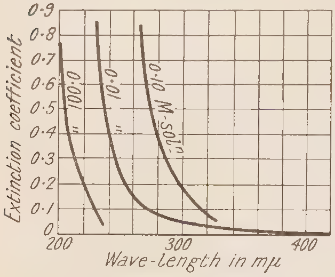


FIG. 106.—Effect of Wave-length on the Extinction Coefficient of Solutions of Potassium Perdisulphate.

Dil. soln. of perdisulphuric acid were found by K. Elbs to be fairly stable, but they are slowly hydrolyzed first to permonosulphuric and sulphuric acids; and then to hydrogen dioxide and ozonized oxygen. A. von Bäyer and V. Villiger, for instance, found that in a fresh soln. of persulphuric acid in sulphuric acid, there was present 98·95 per cent. of the active oxygen as $H_2S_2O_8$, and 1·05 per cent. is H_2SO_5; after 8 days, these proportions were 93·87 and 6·13, and no hydrogen dioxide could be detected in the liquid. K. Elbs and O. Schönherr observed in another specimen:

Time . .	0	4	13	32	56 days
$H_2S_2O_8$.	510	487	411	39	— grm. per litre.
H_2O_2 . .	—	trace	trace	7·0	3·8 "
H_2SO_5 .	129	161	238	605	644 "

The more dil. the soln., the slower the rate of decomposition; the rate of hydrolysis increases with the concentration of the sulphuric acid; and hydrogen dioxide accumulates if a large proportion of sulphuric acid is present. K. Elbs and P. Neher said that sodium, potassium, and ammonium persulphates can be preserved almost unchanged for years if kept dry and protected from sunlight. At ordinary temp., aq. soln. show an appreciable decomposition after some days, and with increasing temp. the rate of decomposition rapidly increases and is further accelerated by sunlight. At 100°, decomposition is practically complete in one hour, although the actual velocity varies to a considerable extent with the conc. of the soln., and with the nature of the cation, the sodium salt being somewhat more stable than the potassium and ammonium salts. The addition of sodium sulphate distinctly diminishes the velocity of decomposition, whilst the presence of 5 per cent. of sulphuric acid accelerates decomposition five to ten times. As an oxidizing agent, sodium persulphate is the most useful salt, and it is often advantageous to diminish the velocity of the reaction, and so prevent loss of available oxygen evolved as gas, by adding about 20 per cent. of anhydrous sodium sulphate to the soln. N. R. Dhar observed that substances with high temp. coeff. for their thermal reactions are often sensitive to light, and in accord with this aq. soln. of potassium perdisulphate are decomposed by exposure to light. J. L. R. Morgan and R. H. Crist showed that the photochemical decomposition of aq. soln. proceeds at 30° similar to the thermal decomposition: $K_2S_2O_8+H_2O=2KHSO_4+\frac{1}{2}O_2$, but no evidence of the formation of any intermediate compounds. The photochemical decomposition proceeds according to a zero or linear order in the more conc. soln. with a limited light intensity and according to a unimolecular order in the very dil. soln. The order for the intermediate soln. is an accelerated unimolecular one, the value of the constants depends upon the light intensity and upon the conc. The effect of gases and of the ageing of the lamp has been studied. Varying the concentration of the oxygen produces no change in the rate of the reaction; consequently, the reaction is not reversible. Hydrogen and nitrogen do not accelerate the reaction. Solid potassium persulphate decomposes under ultra-violet radiations. The velocity constant K for unimolecular reactions with light of intensity I, with 0·001M-soln. at 40°, were 0·0060, 0·0093, 0·020, and 0·038 when the intensities of the light were respectively $\frac{1}{40}$, $\frac{1}{20}$, $\frac{1}{10}$, and $\frac{1}{5}$. The velocity is proportional to the intensity of the light since kI is virtually constant. The wave-length effective in producing the reaction, as well as the region of maximum absorption of light, is in the lower ultra-violet at about $22m\mu$; the value predicted by the radiation theory is 1μ. The temp. coeff. of the photochemical decomposition has the average value 1·18, which low value is further evidence of the simplicity of the reaction. Within the limits of experimental error it is the same for acid, alkaline, and alkaline potassium sulphate soln. in full or in filtered light. J. L. R. Morgan and R. H. Crist found that the rate of photochemical decomposition is retarded by additions of potassium hydroxide, potassium sulphate, and sulphuric acid. O. Risse, and A. K. Bhattacharya and N. R. Dhar studied the photochemical decomposition of the persulphates.

As observed by H. Marshall, M. Berthelot, and R. Löwenherz, the **thermal decomposition** of perdisulphuric acid is accelerated by a rise of temp., but the last traces can be destroyed only by a prolonged boiling of the soln. C. Marie and L. J. Bunel found that the presence of a little methyl alcohol hastens the decomposition. If, then, the soln. be boiled, and the liquid titrated with standard alkali, the persulphate originally present in the soln. can be calculated: $K_2S_2O_8+H_2O=K_2SO_4+H_2SO_4+O$. This was done by C. Marie and L. J. Bunel, A. Kailan and L. Olbrich, N. Tarugi, and C. A. Peters and S. E. Moody. According to M. Mugdan, the velocity of transformation of perdisulphuric acid, dissolved in a large excess of sulphuric acid, into permonosulphuric acid is proportional to the conc. of the perdisulphuric acid, so that the reaction is unimolecular in accord with $H_2S_2O_8+H_2O=H_2SO_5+H_2SO_4$. The velocity constants are not very satisfactory because of the varying conc. of the sulphuric acid; the higher the conc. of the sulphuric acid, the higher their numerical value. L. Green and O. Masson showed that the velocity constant is dependent on the initial concentration, so that it varies in different experiments, but is constant in any one of them. Assuming that the reaction proceeds according to the equation $S_2O_4''+H_2O=2HSO_4'+\frac{1}{2}O_2$, and that it is accelerated by the $H^{\cdot}$-ions initially present, and which remain unchanged in concentration during the reaction, the accelerating influence of $H^{\cdot}$-ions is explained by assuming that at the dilutions employed, the great bulk of the persulphuric acid is completely ionized into $2H^{\cdot}$ and S_2O_8'', while a small proportion is converted into $H^{\cdot}$ and HS_2O_8'. If this proportion be small enough, the total $H^{\cdot}$ concentration may be taken as constant and equal to $2A$, whilst that of the S_2O_8'' is appreciably equal to $A-x$, and that of the HS_2O_8' itself is therefore proportional to $A(A-x)$. If, further, the HS_2O_8' has a sufficiently high rate of reaction as compared with the S_2O_8'', it will make itself felt in spite of its small concentration, and the total velocity of the action will be the sum of two velocities, $k_2(A-x)$ and $kA(A-x)$, in accordance with the equation already given. The resulting velocity equation assumes the form: $dx/dt=(k_2+k_1a)(a-x)$, where k_2+k_1a is a constant k in any given experiment; a is the initial conc. of the perdisulphuric acid—mols per litre—and $a-x$, its conc. at any subsequent time t. Comparing experiments with different values of a, it followed that $k_1=0{\cdot}163$, and $k_2=0{\cdot}010$. It was also found that, at 80°, for

a . . .	0·2566	0·1251	0·1237	0·0923	0·0644	0·0416
K (obs.). .	0·0527	0·0304	0·0302	0·0258	0·0210	0·0184
k (calc.). .	0·0518	0·0304	0·0302	0·0250	0·0205	0·0168

The effect of temp. is such that when $a=0{\cdot}124$ at 70°, $k=0{\cdot}0111$, and at 80°, 0·0302, and when $a=0{\cdot}116$ at 90°, $k=0{\cdot}1035$. The results were confirmed by observation on the effect of admixtures with nitric acid, and sulphuric acid of different concentration. With added sodium perdisulphate, or sodium nitrate, the $Na^{\cdot}$-ions as well as the $H^{\cdot}$-ions exert a specific effect. T. S. Price and A. D. Denning found that the rate of decomposition of $15{\cdot}5N\text{-}H_2S_2O_8$ in the presence of $1{\cdot}4N\text{-}H_2SO_4$ is practically unaffected by colloidal platinum. A. Kailan discussed the decomposition of potassium persulphate by exposure to radium rays.

Soln. of the perdisulphates gradually decompose: $K_2S_2O_8+H_2O=2KHSO_4+\frac{1}{2}O_2$. The oxygen is more or less ozonized. N. Tarugi, and M. G. Levi and E. Migliorini showed that potassium and sodium perdisulphates decompose in aq. soln. unimolecularly, and that the action is much accelerated by the addition of acids. The reaction itself produces an increasing acidity in the soln. so that the velocity should show the characteristics of an auto-accelerated reaction rather than those of a simple unimolecular reaction. L. Green and O. Masson showed that the difficulty disappears if it be assumed that the acid sulphate produced ionizes only into metal and HSO_4'-ions, and provides practically no $H^{\cdot}$-ions; otherwise expressed, that the sulphuric acid behaves like a monobasic acid: $Na_2S_2O_8+H_2O=2NaHSO_4+\frac{1}{2}O_2$, or $S_2O_8''+H_2O=2HSO_4'+\frac{1}{2}O_2$. With the same notation as before, for a soln. of sodium perdisulphate at 80°, $dx/dt=k(a-x)$, and for $a=0{\cdot}226$, $k=0{\cdot}00541$; for $a=0{\cdot}125$, $k=0{\cdot}00577$; and for $a=0{\cdot}127$, $k=0{\cdot}00533$. Again, for $a=0{\cdot}125$ at 70°, $k=0{\cdot}0016$; for $a=0{\cdot}126$ at 80°, $k=0{\cdot}0055$; and for $a=0{\cdot}130$ at 90°, $k=0{\cdot}0161$. Similarly, with potassium perdisulphate, for $a=0{\cdot}108$ at 80°, $k=0{\cdot}00541$; and with ammonium perdisulphate, for $a=0{\cdot}229$ at 80°, $k=0{\cdot}0061$. The result with ammonium sulphate was rather more irregular than with the other salt; this was attributed to the formation of traces of nitric acid, by oxidation of the ammonia. Analogous results were obtained with sodium perdisulphate admixed with sodium hydrosulphate, sodium sulphate or sulphuric acid. The case of barium perdisulphate differs from those indicated above owing to the precipitation of barium sulphate, $2BaS_2O_8+H_2O=H_2S_2O_8+2BaSO_4+\frac{1}{2}O_2$. As a result the xt-curve is at first concave, indicating a marked autocatalysis in the soln. This part of the reaction occurs in two stages $S_2O_8''+H_2O=2HSO_4'+\frac{1}{2}O_2$ followed by $2Ba^{\cdot\cdot}+2HSO_4'=2BaSO_4+2H^{\cdot}$. The first of these two stages is relatively slow, the second fast. The second part of the reaction involving the decomposition of persulphuric acid proceeds unimolecularly as indicated above. If the total conc. of the S_2O_8 radicle at the time t is $a-x$, that of the barium perdisulphate will be $a-2x$; and that of the perdisulphuric acid x. If k_3 be the velocity constant for barium perdisulphate; k_2, that for persulphuric acid; and k_1, that for the catalytic $H^{\cdot}$-ions produced in the reaction, the velocity equation for the barium perdisulphate part of the reaction is:

$$\frac{dx}{dt}=\left(k_3\frac{a-2x}{a-x}+k_2\frac{x}{a-x}+k_1x\right)(a-x)$$

It was found that $k_3=0{\cdot}0040$; $k_2=0{\cdot}010$; and $k_1=0{\cdot}163$, and the observed and calculated results are in agreement. Confirmatory observations were also made with mixtures of barium perdisulphate respectively with nitric acid and with barium nitrate. M. G. Levi and E. Migliorini said that the presence of alkali hydroxide exerts a marked accelerating action on the decomposition of the persulphates, but L. Green and O. Masson showed that the velocity constant with the added alkali hydroxide is very slightly smaller, and that this is accounted for by the physical effect of the extra solute, but there is no evidence of positive or negative acceleration by hydroxyl ions. M. G. Levi and E. Migliorini found that platinum-black slowly catalyzes the decomposition of soln. of the perdisulphates; the greatest effect being produced with ammonium perdisulphate. Lead and some other metals also decompose the soln. catalytically. T. S. Price observed that colloidal platinum does not decompose soln. of slightly acidic or neutral potassium or ammonium perdisulphate. A. Kailan and E. Leisek studied the velocity of decomposition of sodium persulphate, alone and with the addition of sodium hydrogen sulphate, sodium sulphate, nitrate, or hydroxide, phosphoric acid, disodium hydrogen and trisodium phosphates, or potassium hydroxide, and of potassium persulphate, alone and with the addition of potassium nitrate, potassium and sodium hydroxides, has been studied at 99·4°. In the autodecomposition of sodium persulphate the value of the unimolecular coefficient decreases with increasing original conc.; the values found are 2 to 8 per cent. higher than those for potassium persulphate. The addition of a neutral sulphate causes a larger decrease in the coeff. than an admixture of sulphuric acid. On comparing the rates of decomposition of sodium and potassium persulphates with added sodium or potassium sulphate, it follows that sodium ions retard the decomposition of the persulphate ions to a smaller extent than potassium ions. This is verified by the fact that increasing conc. of added sodium hydroxide to sodium persulphate causes an increase in the velocity of decomposition to a greater extent than potassium hydroxide. Nitrate and phosphates accelerate decomposition. In the series of sodium persulphate decompositions the agreement between the observed unimolecular coefficients and those calculated from an intrapolation formula expressed as a function of the conc. of sodium, nitrate, hydroxide, and phosphate (HPO_4'') ions, and the difference between the hydrogen- and sulphate-ion conc., is fairly good. With a mixture of a $0{\cdot}1N$-soln. of potassium persulphate with $0{\cdot}3N$-H_2SO_4, the permonosulphuric or Caro's acid can be qualitatively detected. In 2·7 or $14N$-sulphuric acid the amount of hydrogen dioxide present is 1 to 2 or 6 to 12 per cent. of the then existing Caro's acid. The unimolecular velocity coeff. for the decomposition of persulphuric acid, with or without formation of Caro's acid, is a function of the sulphuric acid conc.

The persulphates so far discovered are all soluble in **water,** the potassium salt is one of the least soluble. A. R. Forster and E. F. Smith showed that in the series: K, Rb, Cs, Tl, the solubility increases with increasing at. wt. The hydrolytic action of water in breaking down perdisulphuric acid to permonosulphuric acid and to hydrogen dioxide has been previously discussed. A. Pietzsch and G. Adolph based a process for the preparation of hydrogen dioxide on this reaction. T. S. Price showed that potassium perdisulphate probably reacts very slowly with **hydrogen dioxide** in aq. soln., the reaction being represented by the equation. $H_2O_2+K_2S_2O_8=2KHSO_4+O_2$. J. H. Kastle and A. S. Loevenhart said that potassium perdisulphate is transformed by hydrogen dioxide into the salt of permonosulphuric acid, which, under the influence of colloidal platinum, gives off oxygen, and reforms the perdisulphate. T. S. Price said that the speed of decomposition of hydrogen dioxide by platinum is only slightly increased by the addition of persulphates. T. S. Price and A. D. Denning said that the acceleration of the speed of decomposition by colloidal platinum is probably proportional to the amount of persulphate added; the effect of the persulphate is mainly catalytic, for it is itself only slightly decomposed. The decomposition of hydrogen dioxide is also accelerated by free persulphuric acid, but the latter is itself decomposed, probably by interaction with the hydrogen dioxide: $H_2O_2+H_2S_2O_8=2H_2SO_4+O_2$—*vide infra*, the action of permanganates. According to J. A. N. Friend, the reaction with the persulphates in the absence of platinum is probably unimolecular, and there is an unstable intermediate compound formed, $mH_2O_2+nK_2S_2O_8\rightleftharpoons(H_2O_2)_m(K_2S_2O_8)_n$, which was isolated in an impure state. T. S. Price also found that the mol. depression of the f.p. of soln. of hydrogen dioxide with additions of persulphate is smaller than is the case with water. This agrees with the hypothesis that the two compounds unite in soln. H. Palme showed that the velocity of this reaction increases considerably with decreasing conc. of acid. J. A. N. Friend's observations that the reaction is unimolecular was explained by H. Palme on the assumption that permonosulphuric acid is first formed, and that this reacts with hydrogen dioxide. It is suggested that perdisulphuric acid does not itself react with hydrogen dioxide. According to R. Kempf and E. Oehler, **sodium dioxide** readily reacts with ammonium persulphate. When the dry substances are rubbed together in a mortar, the mixture explodes, producing thick fumes. The same result is obtained by heating the mixture, by passing a stream of carbon dioxide over it, or by the addition of a drop or two of water. The temp. at which the explosion occurs lies between 75° and 140°, and depends on the rate of heating and the amount of moisture present. The gases evolved consist of nitrogen and oxygen, but the proportions vary considerably in different experiments. The mixture is not explosive when the dioxide is replaced by sodium hydroxide, or the ammonium persulphate replaced by ammonium sulphate, sodium persulphate, or a mixture of the two.

Perdisulphuric acid and its salts are powerful oxidizing agents. Soln. of **hydrochloric acid** furnish chlorine; **chlorides,** chlorine; **bromides,** bromine; and **iodides,** iodine. According to H. Marshall, with potassium iodide soln., the **iodine** which is liberated in the early stages of the reaction may be oxidized to iodic acid. T. S. Price[4] found that the reaction $K_2S_2O_8+2KI=2K_2SO_4+I_2$ is apparently of the third order, but measurements of the velocity of the reaction agree best with the assumption that the reaction is bimolecular. This probably means that the reaction takes place in stages, one of which governs the order of the reaction, while the other stages proceed comparatively quickly with $\frac{1}{30}$ to $\frac{1}{300}N$-soln.; there is no evidence in favour of the assumption, favoured by B. Merk, that the slow reaction is the reduction of the perdisulphate to permonosulphate: $K_2S_2O_8+H_2O=KHSO_4+KHSO_5$, and the subsequent liberation of iodine by the permonodisulphate; nor is it likely that the anomaly is due to the oxidation of the liberated iodine to iodic acid. The reaction is very sensitive to the catalytic influence of various salt soln. There is a very marked acceleration of the reaction by copper and ferrous salts. In the case of these salts, the acceleration is proportional to the concentration. The acceleration produced by a two and a half millionth M-soln. of ferrous sulphate in the presence of $\frac{1}{32000}M$-$CuSO_4$, or *vice versa*, can be readily detected. Salts of nickel and cobalt cause a slight acceleration, but chromic acid, potassium dichromate, manganese sulphate, sodium nitrite, zinc sulphate, magnesium sulphate, and potassium sulphate were inactive. Mixtures of ferrous and copper sulphates were found to cause an acceleration almost double that calculated additively, so that the catalytic effect of each is increased by the presence of the other. Inactive compounds, such as zinc sulphate, have no effect on the catalysis caused by copper sulphate, but decrease the influence of ferrous sulphate. The addition of acid at first causes a decrease in the catalytic effect of copper sulphate, but a constant value is soon reached. A. von Kiss and L. von Zombory found that allowing for the triiodide equilibrium, the reaction between an iodide and a persulphate is of the second order involving the measurable reaction: $S_2O_8''+I'=S_2O_8I''$, and the rapid reaction: $S_2O_8I''+I'=2SO_4+I_2$. The speed of the reaction is augmented by neutral salts. With ferrous or copper salts, new reaction paths are opened up; thus, with ferrous salts, there is the measurable reaction: $Fe^{\cdot\cdot}+S_2O_8''=FeS_2O_8$, and the two rapid reactions: $FeS_2O_8+Fe^{\cdot\cdot}$

$=2Fe^{\cdot\cdot\cdot}+2SO_4''$, and $2Fe^{\cdot\cdot\cdot}+2I'=2Fe^{\cdot\cdot}+I_2$. A similar scheme explains the action of the copper salts. The effect of neutral salts is here negative. In the presence of acids, the rate of the reaction is slightly lowered; and in the absence of catalytic agents, the reaction is favoured by light. J. N. Brönsted, and A. von Kiss and V. Bruckner studied the action of neutral salts on the reaction between potassium iodide and persulphate. W. Federlin also studied the catalytic effect of iron and copper salts. R. Namais recommended the volumetric determination of persulphates by adding an excess of potassium iodide, allowing the mixture to stand 12 hrs., and titrating back the liberated iodine with a standard sodium thiosulphate soln. The reaction was studied by G. Allard, C. A. Peters and S. E. Moody, G. H. Mondolfo, F. G. Soper, A. von Kiss, A. von Kiss and L. Hatz, E. Jette and C. V. King, W. Oostveen, etc. M. Dittrich and H. Bollenbach found that the alkali chlorides, bromides, or iodides are oxidized to chlorates, bromates, or iodates respectively when treated with a nitric acid soln. of a persulphate in the presence of silver nitrate. S. O. Rawling and J. W. Glassett found that the speed of the reaction between potassium iodide and persulphate is accelerated by the presence of gelatin; it is increased by acids; and decreased by alkalies. The effect of the gelatin is attributed either to an organic catalyst in the gelatin, or to the adsorption of the reacting ions by the gelatin particles. B. K. Mukerji and N. R. Dhar, and A. K. Bhattacharya and N. R. Dhar studied the photochemical reaction between potassium iodide and persulphate. E. Müller and W. Jacob examined the interaction of persulphates and **iodates** resulting in the formation of sulphates and periodates.

D. Vitali[5] said that **hydrogen sulphide** causes a turbidity when warmed with a persulphate soln. W. Traube found that persulphates absorb **sulphur trioxide** and at the same time lose some of their active oxygen, forming what he called *perpyrosulphates:* $K_2S_2O_8+2SO_3=KS_2O_6.O_2.S_2O_6K$. These compounds, typified by the potassium salt—**potassium pertetrasulphonate,** $KO.SO_2.SO_2.O.O.SO_2.SO_2.OK$ —fume in the air, the fumes not consisting, however, of sulphur trioxide, and they gradually deliquesce. No oxygen is evolved during the deliquescence, and the soln. formed contains considerable quantities of hydrogen dioxide and persulphuric acid in varying proportions. When put into water the salts dissolve with violent hissing, and ozonized oxygen is evolved; the soln. formed contains only traces of hydrogen dioxide and persulphuric acid. A. Bach found that when anhydrous **sulphuric acid** is mixed with well-dried potassium persulphate there is evidence of the formation of *Ueberschwefelsäure oder Peroxydschwefelsäure—vide infra,* potassium permanganate. According to H. Palme, when persulphuric acid is warmed with sulphuric acid, it decomposes with formation of Caro's acid and hydrogen peroxide: $H_2S_2O_8+H_2O=H_2SO_5+H_2SO_4$; $H_2SO_5+H_2O=H_2O_2+H_2SO_4$. Both reactions are unimolecular, and their velocity is increased with increasing concentration of sulphuric acid. The velocity of the first reaction is about 39 times that of the second at 50°. H. Marshall found that when a slight excess of a persulphate is allowed to react with a **thiosulphate,** a tetrathionate is formed in accord with $2M_2S_2O_3+M_2S_2O_8=2M_2SO_4+M_2S_4O_6$, and the reaction is attended by the evolution of much heat. If an excess of thiosulphate is employed, trithionates are formed owing to the removal of sulphur from the tetrathionate by the excess of thiosulphate or of its decomposition products since the soln. becomes faintly acid. For a time, potassium persulphate was placed on the market, under the trade-name *anthion,* for use as a hypo-eliminator in photography, but the tetrathionate produced was found to be just as objectionable as the thiosulphate, and the silver image was itself attacked. M. G. Levi and co-workers found that **selenium,** and **tellurium** pass into soln. of potassium persulphate as anions.

According to M. G. Levi and E. Migliorini,[6] when aq. soln. of ammonium persulphate are heated at 50°–100°, oxidation occurs even in soln. originally neutral, and the soln. become more and more acid, owing to the liberation of sulphuric acid. Less than the theoretical amount of oxygen is evolved, and nitric acid is formed in soln. The addition of increasing amounts of sodium hydroxide to the persulphate soln. causes the oxidation at first to diminish to a minimum, and then to increase indefinitely. H. Marshall and J. K. H. Inglis represented the reaction in the presence of silver salts: $8(NH_4)_2S_2O_8+6H_2O=7(NH_4)_2SO_4+9H_2SO_4+2HNO_3$. In the presence of **ammonia,** and a silver salt, H. Marshall found that there is no deposition of silver peroxide, but there is a rapid evolution of nitrogen owing to the oxidation of ammonia by the silver peroxide; the action may be very violent in conc. soln. The silver salt acts catalytically on the reaction: $3(NH_4)_2S_2O_8+8NH_3=N_2+6(NH_4)_2SO_4$. D. M. Yost found that the rate of oxidation of ammonia to nitrogen by the persulphate is directly proportional to the conc. of the persulphate ion and the assumed silver triammine ion; the rate also increases with the conc. of the ammonia, and decreases with that of the hydroxide ion—but not directly proportional to the former, nor inversely proportional to the latter. It was assumed that the oxidation process: $2S_2O_8''+2NH_3=4SO_4''+N_2+6H^{\cdot}$ proceeds by the slow stage $S_2O_8''+Ag(NH_3)_3{}^{\cdot}=2SO_4''+Ag^{\cdot\cdot\cdot}+3NH_3$; followed by the fast reactions $3Ag^{\cdot\cdot\cdot}+8NH_3=3Ag(NH_3)_2{}^{\cdot}+N_2+6H^{\cdot}$, and $Ag(NH_3)_2{}^{\cdot}+NH_3=Ag(NH_3)_3{}^{\cdot}$. The velocity equations are $-d[S_2O_8'']/dt=k_1[S_2O_8''][Ag(NH_3)_2{}^{\cdot}]+k_2[S_2O_8''][Ag(NH_3)_3{}^{\cdot}]$, where $[Ag(NH_3)_3{}^{\cdot}]=K[Ag(NH_3)_2{}^{\cdot}]$-$[NH_3]$. These reduce to $-d[S_2O_8'']/dt=[S_2O_8''][Ag(NH_3)_2{}^{\cdot}]\{k_1+k_2K(NH_3)\}$ which agrees with the observed results, where $k_1=3{\cdot}70$, and $k=\{k_1+k_2K(NH_3)\}=4{\cdot}5$ nearly. R. Kempf said that 88 per cent. of the ammonium salts in some commercial sodium persulphate was oxidized to nitric acid when the soln. in soda-lye was kept 4 days at ordinary temp., and 40 per cent. was oxidized to nitric acid when the soln. was boiled. When the silver peroxide is in contact with the persulphate and ammonia for several days no oxygen is evolved, and the persulphate is converted into nitric acid: $8Na_2S_2O_8+6H_2O+(NH_4)_2SO_4=16NaHSO_4+H_2SO_4+2HNO_3$. If the silver salt be absent, persulphates do not bring about the oxidation which must be due to the silver peroxide, and not to ozone, hydrogen dioxide, or permonosulphuric acid. The oxidation is not quantitative. R. Kempf and E. Oehler said that the fact that when an aq. alkaline soln. of ammonium persulphate is kept for some time the ammonia formed is quantitatively oxidized to nitric acid, whereas when silver peroxide is present the main oxidation product is nitrogen, is accounted for by the different velocities of the two reactions, the latter being much more rapid than the former. If the first reaction is accelerated by raising the temp., nitrogen is also formed. The effect of silver salts as catalysts was studied by C. V. King. L. Santi observed that **ammonium chloride** yields nitrogen and chlorine, or even hypochlorous acid. E. Pannain found that when **hydrazine** is liberated from its salts by conc. potash-lye, there is a vigorous reaction: $2K_2S_2O_8+N_2H_4.H_2SO_4+6KOH=5K_2SO_4+N_2+6H_2O$. D. M. Yost found that the rate of oxidation by persulphuric acid, in the presence of a silver salt, is proportional to the conc. of the S_2O_8''-ions and the $Ag(NH_3)_2{}^{\cdot}$-ions; but is only slightly affected by the conc. of the ammonia, and of the OH'-ions. The increase caused by ammonia is probably due to the formation of $Ag(NH_3)^{\cdot}$-ions, which are more active, and OH'-ions may decrease the rate of forming non-ionized $Ag(NH_3)OH$. As indicated in connection with **phosphorous acid**—**8**. 50, 17—this acid is oxidized by potassium persulphate with iodine as catalyst. The phosphorous acid oxidation is a very slow process, without the iodine; the oxidation in the presence of potassium iodide is a consecutive process involving the liberation of iodine from potassium iodide, and the subsequent oxidation of the phosphorous acid. The observed results agree with those calculated from the theory of consecutive reactions. There is a period of induction, and the reaction between the persulphate and iodide is accelerated by copper or ferrous salts. M. G. Levi and co-workers found that **arsenic** passes into soln. as an anion when treated with a soln. of potassium persulphate, while **antimony** and **bismuth** form insoluble oxides. B. Grützner determined the persulphates by reducing the persulphate in an excess of a boiling alkaline soln. of **arsenic trioxide,** and titrating the excess with iodine soln.

H. Marshall[7] and co-workers showed that many organic colouring agents like **indigo, tumeric,** and **litmus** are slowly bleached by acidic or alkaline soln. of persulphates, while **paper** and **cloth** become quite rotten after being dipped in a soln. of potassium persulphate. The activity of ammonium persulphate is greatly enhanced in the presence of silver nitrate, thus **methyl orange** and indigo are bleached. R. Kempf showed that **benzene** in the presence of nitric acid and silver nitrate is oxidized to quinone; and **quinone,** in turn, to maleic acid and carbon dioxide together with formic acid and carbon dioxide; **oxalic acid** is quantitatively converted to carbon dioxide without the silver salt. K. Elbs and O. Schönherr found that the oxidation in acidic or alkaline soln. is incomplete. P. C. Austin found that in the presence of a silver salt, **toluene** is oxidized to benzaldehyde and benzoic acid, and **thymol** forms dithymol—G. G. Henderson and R. Boyd obtained indefinite results with persulphate in alkaline soln. C. Moritz and R. Wolffenstein found that with the **aromatic hydrocarbons** not only are the alkyl groups attacked to form carboxylic or aldehydic groups, but hydrogen is removed and the molecules condensed in pairs. Thus toluene forms benzaldehyde and dibenzyl: $2(C_6H_5.CH_3)+H_2S_2O_8=C_6H_5.CH_2.CH_2.C_6H_5+2H_2SO_4$; ethylbenzene forms dimethyldibenzyl and phenylacetaldehyde; *o*-xylene forms diorthomethyldibenzyl; etc. N. Tarugi found **potassium cyanide** and persulphate in alkaline soln. in the presence of an excess of ammonia react whereby 75 per cent. of the cyanide is converted into carbamide by way of potassium cyanate; and E. Schwarzenauer, and M. Dittrich and C. Hassel found that complex cyanides like **potassium ferro- and ferricyanide** are decomposed by persulphates in the presence of a mineral acid, forming hydrogen cyanide and small amounts of ammonium salts. I. Bellucci and B. Ricca found that when persulphates are heated with potassium ferrocyanide, the hydrogen cyanide evolved is partly oxidized to cyanogen. H. Marshall, and R. Namais found that when **alcohol** is heated with a persulphate to 70°–80° aldehyde is formed. M. A. Gordon found that when a soln. of sodium persulphate is heated with **acetic acid,** or **sodium acetate,** carbon dioxide and one or more hydrocarbons—methane, ethane, and olefines—are produced, for simultaneously with the oxidation, there is the catalyzed reaction: $CH_3.COOH=CH_4+CO_2$. R. Namais showed that many organic compounds capable of oxidation, particularly closed chain compounds, give up hydrogen, and yield sulphonic derivatives—*e.g.* **quinol** forms an insoluble sulpho-compound; while **diaminophenol,** *p*-**phenylenediamine,** and *p*-**aminophenol** give a characteristic colour reaction. When a persulphate is added to a cold soln. of **aniline hydrochloride,** a dark green precipitate is formed, which is insoluble in water or alcohol, and when treated with a soln. of sodium hydroxide or carbonate, turns dark green, but remains insoluble. K. Elbs found that ammonium persulphate introduces a hydroxyl-group directly into the benzene nucleus—*e.g.* *o*-**nitrophenol** in alkaline soln. forms nitrohydroquinone: T. Kumagai and R. Wolffenstein found that *p*-**cresol** in neutral soln. gives dihydroxydibenzyl; in alkaline soln., 3 : 4 dihydroxytoluene; and in acidic soln., 2 : 5 dihydroxytoluene is formed and the methyl group migrates to the ortho-position; and Chemische Fabrik auf Actien vorm. R. Schering found that **salicylic acid** gives 2 : 5 or 2 : 3 dihydroxybenzoic acid; Farbenfabriken vorm. F. Bayer, that **hydroxyanthraquinone** gives alizarine, and **alizarine,** purpurine. N. Caro, and the Badische Anilin- und Sodafabrik showed that in acidic soln., **aniline** furnishes aniline black or emeraldine; in alkaline soln., azobenzene and phenylquinonediimide are formed; and in neutral soln., an orange-brown precipitate is produced. According to L. Hugounenq, **uric acid** is oxidized by ammonium persulphate at the ordinary temp., and converted into allanturic acid, carbamide, and glycine. In presence of an alkali hydroxide, the reaction is more energetic, but the products are carbamide and ammonium allanturate, the action being similar to that of lead or managnese peroxides, potassium permanganate or ferricyanide, or ozone. Allantoin is probably formed as an intermediate product, but if the proportion of persulphate is reduced with a view to isolate it, the greater part of the uric acid remains unaltered. **Bilirubin** in presence of an alkali is completely and instantly converted into biliverdin, and the reaction affords the best method of preparing the latter. **Hæmatin** in presence of ammonia is attacked in the cold, and after boiling for two or three minutes, the black solution becomes colourless and a precipitate of ferric hydroxide is formed. This reaction can be utilized for the detection of iron in hæmatin and probably also in hæmoglobin and the ferruginous nucleins. **Blood** diluted and mixed with excess of ammonia is oxidized and decolorized after a few hours at the ordinary temp. with production of a pale yellow liquid and a slight ochreous precipitate. The same change is produced in a few minutes on heating. E. Seel studied the oxidation of **aloin** by potassium persulphate and obtained what was thought to be aloin red. Many **alkaloids** give characteristic colour reactions—*e.g.* D. Vitali showed that **strychnine** is precipitated as insoluble strychnine persulphate, $(C_{21}H_{22}O_2N_2)_2H_2S_2O_8.H_2O$, and hence ammonium persulphate has been recommended as an antidote in strychnine poisoning.

According to B. Moreau,[8] the persulphates exert a favourable influence on metabolic processes, they stimulate the appetite; and they revive the strength of invalids in a manner similar to arsenites and vanadates, but they are less toxic. They have also been recommended as antiseptics. D. Vitali, however, observed that the antiseptic action of the persulphates is small, and in large doses they are poisonous. N. Tarugi found that the per-acids associated with products found in living organisms can dissolve mercury and calomel. S. Sawa observed that soln. with 0·01 per cent. of persulphate act banefully on plants.

M. G. Levi [9] and co-workers observed the corrosive action of soln. of the persulphates on **titanium**; and A. Bach found that in sulphuric acid soln., the persulphates do not give with **titanium salts** the yellow coloration characteristic of hydrogen dioxide; if sulphuric acid be anhydrous, the yellow coloration may be produced although no hydrogen dioxide is present. E. Knecht and E. Hibbert found that ammonium persulphate oxidizes a soln. of **titanium trichloride** quantitatively, and if an excess of the latter has been added, the excess can be titrated with a soln. of a ferric salt and the persulphate accordingly determined.

H. Marshall [10] found that soln. of potassium persulphate dissolve many of the **metals** illustrating the case of a metal dissolving in a soln. of a normal salt producing a soln. containing only normal salts. A. Bringhenti, and M. G. Levi and co-workers stated that all the metals they examined—Cu, Ag, Au, Mg, Zn, Cd, Hg, Al, Ti, Sn, Pb, As, Sb, Bi, Cr, Se, Te, U, Mn, Fe, Ni, Co, Pd, Pt—excepting gold and platinum, react with the persulphate soln., either passing directly into soln. or remaining undissolved in the form of oxides or basic salts. In general, the reaction is slower for ammonium than for potassium persulphate, probably owing to the slightly greater degree of dissociation of the potassium salt; in the catalysis with platinum, the tendency is in the opposite direction. In general, those metals go into soln. as anions which in their general chemical behaviour exhibit a marked non-metallic character, such as chromium, manganese, selenium, arsenic, molybdenum, etc.; some metals of this type, however, such as antimony, are transformed into insoluble oxides. The general action with these metals is hence oxidation by the persulphate with intervention of water. Elements which are distinctly metallic in character pass into solution as cations, the persulphate being decomposed, sometimes with evolution of gas. With zinc, nickel, cobalt, etc., no gas is evolved, and in these cases the reaction is probably represented by $Zn+X_2S_2O_8=ZnSO_4+X_2SO_4$, or by (i) $Zn+X_2S_2O_8+H_2O=ZnO+H_2SO_4+X_2SO_4$, and (ii) $ZnO+H_2SO_4=ZnSO_4+H_2O$; according to the latter interpretation, the solution may remain neutral or become acid, this depending on the relative velocities of both the reactions. When gas is evolved, this is found to be hydrogen, at any rate for conc. persulphate soln. The reactions studied are, except in the cases of gold and platinum, more chemical than catalytic in nature. They proceed with different velocities for different metals, although the velocity does not always bear any evident relation to the oxidizability of the metal, or to its readiness to attack by sulphuric acid. The tendency to form double salts or complexes doubtless plays a part. H. Marshall found that with copper, a soln. of cupric sulphate is formed, and a slight reddish deposit is formed on the metal, $(NH_4)_2S_2O_8+Cu=CuSO_4+(NH_4)_2SO_4$—M. G. Levi and co-workers added that there is a slow evolution of gas. R. Namais said that copper is not attacked by neutral or acidic soln. of the persulphates, but is rapidly attacked in the presence of ammonia. J. W. Turrentine found that copper behaves in ammonium persulphate soln. like a copper anode in a soln. of ammonium sulphate. R. Namais found that silver is gradually dissolved by either acidic or ammoniacal soln. of the persulphates. H. Marshall added that the reaction may be used in place of nitric acid for etching copper or silver. According to E. Groschuff, copper and copper alloys, in which the percentage of copper is predominant, can be coloured black by heating the metal for some minutes at 100° in a 5 per cent. soln. of sodium hydroxide to which one per cent. of potassium persulphate is added from time to time until the desired colour is obtained. For brass and aluminium bronze, a 10 per cent. soln. of soda-lye is used. H. Marshall observed that silver is gradually corroded: $K_2S_2O_8+2Ag=K_2SO_4+Ag_2SO_4$, and by a second reaction a black deposit of silver peroxide is formed: $Ag_2SO_4+K_2S_2O_8+H_2O=K_2SO_4+2H_2SO_4+Ag_2O$; gold is not attacked. According to G. I. Higson, a soln. of sodium or potassium persulphate converts silver into a peroxide containing a greater proportion of oxygen than corresponds with the formula Ag_2O_2, whilst the acidity of the soln. at the same time increases. When a conc. (20 per cent.) soln. of the sodium salt is used, the peroxide can rapidly be obtained in quantity, but owing to the much smaller solubility of the potassium salt the reaction with this is much slower (for example, eighteen hours) and the yield much lower, for the peroxide is unstable and decomposes continuously from the time of its formation. With the ammonium salt, no peroxide is formed, but the ammonium radicle is oxidized. When the reaction is continued for more than about one hour, the product is contaminated with sulphate, which is always present to a slight extent. The same peroxide is produced when persulphates react with silver nitrate, again with increase in acidity, but in this case the contamination with silver sulphate is greater. This contamination is due to the catalytic decomposition of persulphates by silver ions, whereby in the case of the sodium and potassium salts, the reaction $S_2O''_8+H_2O\rightarrow 2HSO_4'+O$ is immensely accelerated. The HSO_4'-ions thus formed react continuously with silver-ions, and as these are present in much greater quantity when silver nitrate is used, the amount of silver sulphate formed is consequently greater in this case. Moreover, the catalytic effect increases with increase of conc. of the silver ions, and this again tends to produce more contamination when silver nitrate is used in the preparation. A possible explanation of this catalytic effect is the intermediate formation of silver persulphate, which then immediately reacts with the water: $Ag_2S_2O_8+H_2O\rightarrow Ag_2SO_4+2H^{\cdot}+O+SO_4''$. The presence of an oxidizable substance, such as gelatin, prevents the formation of peroxide, whilst it is itself oxidized; but it does not prevent the catalytic decomposition of the persulphate, with formation of acid sulphate. The reaction in the presence of an oxidizable substance is taken to be $6Ag+8S_2O_8''+5H_2O\rightarrow 6Ag^{\cdot}+6SO_4''+10HSO_4'+5O$. The acidity is not due, as M. G. Levi and co-workers supposed, to the formation of sulphuric acid simultaneously with silver oxide, but rather to the decomposition of the water during the reaction: $S_2O_8''+H_2O\rightarrow 2HSO_4'+O$, where the oxygen goes to the silver. The action of ammonium persulphate on silver has led to its use as a density reducer for negatives, a reaction discussed by H. Marshall, J. W. Dodgson, D. M. Yost, C. V. King, and E. Stenger and G. Heller.

H. Marshall found that magnesium is quietly dissolved by a soln. of potassium persulphate: $K_2S_2O_8+Mg=K_2SO_4+MgSO_4$, but, added M. G. Levi and co-workers, magnesium acts very violently with a soln. of ammonium sulphate, and ammonia is evolved. O. Aschan obtained complex salts by the action of magnesium, zinc, cadmium, iron, nickel, and cobalt on cold, aq. soln. of the alkali persulphates. H. Marshall found that zinc dissolves quietly as in the case of magnesium; and R. Namais also observed that zinc is dissolved by neutral soln. of the persulphates. H. Marshall said that cadmium behaves like zinc; J. W. Turrentine said that cadmium bears out the analogy between chemical corrosion in soln. of ammonium persulphate and electrolytic corrosion in soln. of ammonium sulphate. H. Marshall found that mercury is rapidly attacked, forming a slight black deposit which soon gives way to a yellowish-white precipitate. In the presence of free sulphuric acid, a white precipitate only is produced, and this is also the case with soln. of ammonium persulphate. N. Tarugi also said that mercury is vigorously attacked and especially so by an ammoniacal soln. of ammonium persulphate. If the temp. of the reaction is not allowed to rise above 60°, the liquid deposits ammonium mercurous diamminopersulphate on cooling. The reaction was studied by S. Stern. P. Neogi and R. C. Bhattacharyya found magnesium amalgam reduces persulphates to sulphates. The action of a soln. of potassium persulphate on aluminium was found by H. Marshall to resemble its action on magnesium, or zinc; according to S. E. Sheppard, if a strip of copper, brass, or bronze is dropped into a soln. of potassium persulphate it is blackened readily and completely, whereas if it is slowly lowered into the soln., blackening either does not take place or is merely a patchy tarnish. The oxide layer forms a soft, velvety pile which consolidates when rubbed to a smooth and semi-lustrous layer. The phenomenon is evidently associated only with the difference in the time exposure of the metal to the air-soln. interface, and normal blackening can be caused by mechanical or chemical protection of the metallic surface as it passes the interface where mol oxygen is accumulating as a result of the reaction: $K_2S_2O_8+H_2O=2KHSO_4+O$; and $O+O=O_2$. The formation of a copper peroxide is assumed to cause the oxygen interference, with a subsequent reduction. R. Namais showed that aluminium is dissolved by neutral soln. of the persulphates; and J. W. Turrentine, that the chemical corrosion of aluminium by ammonium persulphate is analogous to its electrolytic corrosion by ammonium sulphate. H. Marshall found that lead is attacked superficially since a protective film of sulphate appears to be formed; cobalt dissolves, forming a pink soln., and a slight, dark-coloured deposit; nickel sheet or wire is slightly attacked, but an electrolytic deposit of the metal dissolves rapidly. J. W. Turrentine observed the analogy between the chemical corrosion of nickel by ammonium persulphate, and its electrolytic corrosion by ammonium sulphate. H. Marshall showed that metallic iron dissolves very easily in soln. of persulphate; with concentrated and slightly acid solution of ammonium persulphate the action is violent. If ordinary iron is used, a deposit of carbon remains. Iron is quickly attacked by the soln., even if it contains free ammonia, ferric hydroxide being formed; and, as it is probable that no carbon compound is produced under such circumstances, this might form a convenient method of obtaining the total carbon in iron analyses. R. Namais also found that iron is dissolved by neutral soln. of the persulphates, and, added J. W. Turrentine, the soln. of iron in ammonium persulphate subsequently deposits ferric sulphate. H. Marshall showed that platinum is not attacked by soln. of the persulphates; and T. S. Price added that with gold and platinum, catalytic reactions, resulting in the decomposition of the persulphate, take place very slowly; while soln. of potassium or ammonium persulphate are not attacked by colloidal platinum.

According to A. Seyewitz and P. Trawitz,[11] when ammonium persulphate reacts with the **metal oxides** the ammonia may be displaced with the formation of the metal persulphate: $2MOH+(NH_4)_2S_2O_8=M_2S_2O_8+2H_2O+NH_3$; or sesquioxides or peroxides may be formed—for instance, this is the case with cobalt and lead hydroxides. With the sesquioxides or peroxides, part of the ammonia may be oxidized and nitrogen evolved, forming the corresponding sulphate—*e.g.* nickel sesquioxide and cupric oxide—or the sulphate is formed and oxygen evolved—*e.g.* the sesquioxides of iron and aluminium, or the peroxides of mercury, cerium, bismuth, and platinum—or complete peroxidation may occur—*e.g.* the hydroxides of chromium and manganese.

H. Marshall said that the most striking properties of the persulphates is their powerful oxidizing action whether in neutral, alkaline, or acidic soln. In many cases, the action is probably not a direct oxidation, for a mol of the persulphate may take up an atom of metal, forming two mols of sulphate. According to D. Vitali, persulphates decompose soln. of the **metal salts**, forming sulphuric acid, sulphate, and oxygen, with the metal chlorides—*e.g.* barium chloride, the hot soln. forms hydrochloric acid which is attacked by the nascent oxygen, forming chlorine, and barium sulphate is precipitated. In some cases, the metal peroxide is formed—*vide infra*, the persulphates. H. Marshall showed that with **silver salts,** a black silver peroxide is formed: $2AgNO_3+K_2S_2O_8=2KNO_3+Ag_2S_2O_8$, followed by $Ag_2S_2O_8+2H_2O=Ag_2O_2+2H_2SO_4$; or $2AgNO_3+K_2S_2O_8+2H_2O=2KHSO_4+2HNO_3+Ag_2O_2$. The product was examined by P. C. Austin, who showed that it is probably a mixture of silver peroxide and persulphate. D. M. Yost supposed it to be a tervalent silver compound; and G. I. Higson made observations on this subject. N. Tarugi supposed that nitrous acid and silver permonosulphate are formed: $2AgNO_3+K_2S_2O_8+H_2O=Ag_2SO_5+K_2SO_5+HNO_2+HNO_3$, while R. Namais said that perdisulphuric acid acts as a reducing agent on silver nitrate. D. Vitali showed that with **barium and strontium salts,** the sulphate is precipitated and oxygen is evolved, and he recommended this as a means of evaluating persulphates. G. von Knorre found that **cerous salts** pass into ceric salts when heated with persulphates, and, unlike hydrogen dioxide, an excess of persulphate in the presence of sulphuric does not discharge the colour. H. Marshall observed that soln. of **lead salts** give a precipitate of lead dioxide only after the soln. has been made alkaline. D. Vitali showed that basic lead acetate with the persulphates gives a precipitate which turns blue when treated with acetic acid and tincture of guaiacum. P. Schoop said that the precipitate obtained by adding ammonium persulphate to lead acetate soln. is lead persulphate, but K. Elbs and O. Schönherr said lead sulphate, and added that the pure persulphate gives no precipitate. J. R. Cain and J. C. Hostetter found that **vanadic salts** (quinquevalent vanadium) in conc. sulphuric acid are reduced by persulphate to the quadrivalent state. H. Marshall found that **chromic salts** are converted into chromates in acidic or alkaline soln. H. D. Dakin also observed that in alkaline soln. the oxidation to chromate is complete, but not so in acidic soln. unless a trace of silver salt be present as catalytic agent as recommended by H. Marshall. It is remarkable that mixtures of conc. nitric acid and potassium persulphate do not convert chromic salts into chromates, a reaction effected by potassium chlorate. The conversion of chromium and chromic salts into chromates by the persulphates is utilized in analytical processes by F. Ibbotson and R. Howden, H. E. Walters, G. von Knorre, M. Dittrich and C. Hassel, R. Namais, H. D. Dakin, etc. The oxidation is complete and can be represented by the irreversible reaction: $3(NH_4)_2S_2O_8+Cr_2(SO_4)_3+7H_2O=3(NH_4)_2SO_4+6H_2SO_4+H_2Cr_2O_7$. When catalyzed by silver salts, D. M. Yost showed that it is probable that a tervalent silver compound is formed as an intermediary: $S_2O_8''+Ag^{\cdot}=2SO_4''+Ag^{\cdot\cdot\cdot}$, followed by $3Ag^{\cdot\cdot\cdot}+2Cr^{\cdot\cdot\cdot}+7H_2O=Cr_2O_7''+3Ag^{\cdot}+14H^{\cdot}$. The first stage is supposed to determine the progress of the whole reaction when the second stage occurs very rapidly. The speed of the oxidation of chromic sulphate at 25° and 30° is proportional to the first power of the conc. of the persulphate and silver ions, but independent of the conc. of the chromic-ion, and not greatly affected by the conc. of the $H^{\cdot}$-ion. Hence, $-d[S_2O_8'']/dt=k[S_2O_8''][Ag^{\cdot}]$, when $k=0{\cdot}333$ at 25°, and $0{\cdot}765$ at 35°. This is in agreement with the assumption that the silver ion acts as a carrier catalyst through the formation of an intermediate silver compound. When a persulphate is treated with **potassium dichromate** and sulphuric acid, and the liquid shaken with ether, unlike the case with hydrogen dioxide, the ether does not turn dark blue. D. Vitali, however, did not agree with this statement. H. Marshall found that when persulphates are added to a soln. of **manganese salts,** manganese dioxide is precipitated. H. D. Dakin showed that the composition of the precipitate varies with the temp., concentration, and proportion of persulphate employed. H. Marshall showed that the oxidation can be carried still further by digesting the mixture on a water-bath for some time, when a pink soln. of permanganic acid or alkali permanganate is slowly formed. The reaction is accelerated in the presence of silver salts. The reaction can then be utilized for the detection or colorimetric determination of manganese. A distinct coloration is produced in half a c.c. of soln. containing 0·001 mgrm. of manganese. The reaction was studied from the analytical point of view by R. Namais, H. D. Dakin, M. Dittrich and C. Hassel, H. Kunze, H. Rubricius, H. E. Walters, H. Wdowiszewsky, W. J. Karslake, J. V. R. Stehman, W. Gottschalk, H. Baubigny, O. Brichant, G. von Knorre, M. Stanichitch, J. J. Boyle, P. Holland, M. R. Schmidt, M. Orthey, etc. H. D. Dakin observed that mixtures of nitric acid and potassium persulphate do not give a precipitate of manganese peroxide from manganous salts, a reaction readily effected by potassium chlorate. Soln. of the persulphate do not decolorize the **permanganates,** and this fact has been utilized to determine hydrogen dioxide in the presence of persulphates. J. A. N. Friend showed that the results vary with the time occupied by the titration, with the conc. of the soln., and the proportion of sulphuric acid it contains. This result is due to a slow reaction between the hydrogen dioxide and the persulphate in the soln. so that for every mol of hydrogen dioxide not accounted for by the permanganate titration, a mol of persulphate disappears: $H_2O_2+K_2S_2O_8=K_2SO_4+H_2SO_4+O_2$. T. S. Price and A. du P. Denning found that the concentrations of both the hydrogen dioxide and potassium permanganate in a mixed soln. gradually diminish. The reactions observed by J. A. N. Friend may occur quickly because of the catalytic action of the manganese salt produced by the reduction of the permanganate, although J. A. N. Friend showed that manganese sulphate does not catalyze the reaction. A. Skrabel regards the effect as a case of induced or sympathetic reactions rather than catalysis *per se.* The reaction was also studied by A. Skrabel and J. P. Vacek, and R. N. J. Saal—*vide infra,* permonosulphuric acid. H. Marshall, and G. von Knorre showed that **ferrous salts** are oxidized to the ferric state: $2FeSO_4+(NH_2)_2S_2O_8=Fe_2(SO_4)_3+(NH_4)_2SO_4$, and if ammonium persulphate is used, ammonium ferric alum will crystallize from the brown soln. The reaction is employed in the determination of persulphates by M. le Blanc and M. Eckardt, where the excess of ferrous salt is titrated with permanganate. H. Marshall observed that when a persulphate is added to a **cobalt salt,** cobalt peroxide is precipitated; F. Mawrow found the composition to be $Co_3O_4.3H_2O$, and if an excess of potash-lye be present, $Co_2O_3.3H_2O$ is formed. A. Coehn and E. Salomon proposed to utilize the reaction for separating cobalt and nickel, for **nickel salts** give a precipitate only after the addition of alkali-lye. L. Tschugaéeff and co-workers studied the oxidation of **platinum salts** by persulphates.

Some reactions of analytical interest.—Many of the tests for persulphates resemble those for hydrogen dioxide; and some of the characteristic reactions previously indicated can be used—*e.g.* the action on aniline or aniline hydrochloride; the action on strychnine; etc. Unlike hydrogen dioxide, the persulphates do not decolorize potassium permanganate, they do not give the yellow coloration with titanium sulphate, or give the perchromic acid reaction with potassium dichromate and sulphuric acid; nor is the yellow colour obtained with cerous salts discharged by an excess of persulphate, although it is with an excess of hydrogen dioxide. A two per cent. alcoholic soln. of benzidine, furnishes a blue colour with persulphates, and this enables one part of persulphate per million to be detected. Conc. soln. of persulphates give a brownish-yellow colour, and also a precipitate which dissolves to a dark yellow liquid. Hydrogen dioxide reacts similarly only in the presence of proteins—*e.g.* milk.[12] The reactions with ferrous sulphate, and potassium iodide can be used quantitatively, and likewise also the hydrolysis to sulphuric acid: $K_2S_2O_8+H_2O=O+K_2SO_4+H_2SO_4$—*vide supra.*

In determining the proportion of hydrogen dioxide, permonosulphuric acid, and perdisulphuric acid in the presence of one another, H. Palme took advantage of the fact that permonosulphuric acid reacts immediately with potassium iodide, whilst hydrogen dioxide reacts much more slowly, and persulphuric acid slowest of all. A sample of the soln. is mixed with potassium iodide and titrated rapidly with sodium thiosulphate, the time taken being noted, so that a correction can be applied for the small quantity of iodine liberated by the hydrogen dioxide and persulphuric acid. The quantity of permonosulphuric acid is thus found. A second sample is then treated with potassium iodide and titrated with sodium sulphite, which reduces hydrogen dioxide. This second titration gives the sum of permonosulphuric acid and hydrogen dioxide. Finally, the persulphuric acid is estimated in a third sample by adding the calculated quantity of sodium sulphite to reduce the other two compounds, and estimating the persulphuric acid by the ferrous sulphate-permanganate method. The dilution for the titrations correspond with 2·0 grms. of potassium persulphate per litre, of which 200 c.c. are titrated at a time.

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§ 35. The Persulphates or Perdisulphates

H. Marshall,[1] and K. Elbs showed that **ammonium persulphate,** $(NH_4)_2S_2O_8$, is the most important salt of perdisulphuric acid, and it is usually the starting point for the preparation of the other salts. Its electrolytic preparation in compartment cells was described by H. Marshall, M. Berthelot, and K. Elbs; and in a cell without a diaphragm, by E. Müller and O. Friedberger—*vide supra.* F. Fichter and K. Humpert found that ammonium persulphate is formed when fluorine acts on a soln. of ammonium hydrosulphite. Ammonium persulphate furnishes white monoclinic crystals which, according to A. Fock, have the axial ratios $a:b:c=1·3001:1:1·1885$, and $\beta=76° 11'$; and the optic axial angle $2E=70°$ nearly. The salt was analyzed by H. Marshall, and J. Möller, and the results agreed with the formula $(NH_4)_2S_2O_8$. The electrical conductivity, and the

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lowering of the f.p. observed by J. Möller, are in agreement with the same formula. A. P. Sabanéeff showed that the salt is isomeric with hydroxylamine dithionate, $(NH_2OH)_2H_2S_2O_6$. J. Möller gave 0·205° for the lowering of the f.p. of water by 1·4131 grms. of the salt in 150·7575 grms. of water. M. Berthelot gave for the heat of formation, (2S,8O,8H,2N)=392·7 Cals.; (2S,8O,8H,2N,Aq.)=383·0 Cals.; $\frac{1}{2}H_2S_2O_8aq.+NH_3aq.=\frac{1}{2}(NH_4)_2S_2O_8aq.+383{\cdot}0$ Cals. The heat evolved when the salt decomposes $(NH_4)_2S_2O_8+H_2O_{solid}=2NH_4(HSO_4)+O+27$ Cals.; $(NH_4)_2S_2O_{8soln.}+H_2O=H_2SO_4+(NH_4)_2SO_4+O+38{\cdot}4$ Cals.; and $(NH_4)_2S_2O_{8soln.}+H_2O=2NH_4(HSO_4)+O+37{\cdot}1$ Cals. The heat of soln. of one part of the salt in 125 parts of water, at 10·5°, is −0·72 Cal., and in 75 parts of water, at 12°, −11·80 Cals. J. Möller gave for the electrical conductivity, μ, of a soln. of an eq. of the salt in v litres of water:

v . .	12·225	12·553	15·528	35·16
μ . .	109·41	112·40	117·66	120·94

According to K. Elbs and P. Neher, sodium, potassium, and ammonium persulphates can be kept for years almost unchanged if dry and protected from sunlight. At ordinary temperatures aq. soln. show appreciable decomposition after some days, and with increasing temp. the rate of decomposition rapidly increases, and is further accelerated by sunlight; at 100°, decomposition is practically complete in about an hour, though the actual velocity varies to a considerable extent with the conc., and the sodium salt is somewhat more stable than the potassium and ammonium salts. The addition of sodium sulphate distinctly diminishes the velocity of decomposition, whilst the presence of 5 per cent. of sulphuric acid increases it 5 to 10 times. G. Agde and E. Alberti found that neither ammonium nor potassium persulphate, nor mixtures of these persulphates with 10 per cent. of organic impurity explode or cause rapid combustion of organic matter when heated at a steady rate. The organic matter is simply charred. Wooden boxes coated with paraffin are recommended for packing the salt for transit. As an oxidizing agent sodium persulphate is the most useful salt, and it is often advantageous to diminish the velocity of the reaction, and so prevent the formation of molecular oxygen, by adding 45 per cent. of crystallized sodium sulphate. According to H. Marshall, ammonium persulphate is very soluble in water; 100 parts of water at 0°, dissolve 58·2 parts of the salt; K. Elbs said that 65 parts are dissolved at room temp.; and B. Moreau, that water, at 8°, dissolves 58 per cent. of the salt. E. Weitz made some observations on this subject. K. Elbs said that if the salt be purified by recrystallization, and dried over calcium chloride, it can be kept for months without perceptible decomposition, but when moist it decomposes at room temp. giving off ozonized oxygen: $(NH_4)_2S_2O_8+H_2O=2NH_4(HSO_4)+O$. The dil. aq. soln. when heated also gives off ozonized oxygen. The aq. soln. gives no precipitate with barium nitrate, but if boiled, barium sulphate is deposited. If treated with potassium carbonate, potassium persulphate is deposited; and when the solid salt is triturated with a conc. soln. of sodium hydroxide or solid sodium carbonate, R. Löwenherz observed the formation of sodium persulphate. H. Stamm studied its solubility in aq. ammonia, and found that soln. with 0, 0·198, 0·700, and 1·008 mols of NH_3 per 100 grms. of water dissolve respectively 0·656, 0·964, 2·108, and 3·038 mols of $(NH_4)_2S_2O_8$. Other reactions have been discussed in connection with the general properties of persulphuric acid.

H. Marshall, and C. N. Otin tried to make **lithium persulphate,** $Li_2S_2O_8$, by the electrolysis of a soln. of lithium sulphate in sulphuric acid at −20°, but although the persulphate was obtained in soln., it could not be separated in the solid form. C. N. Otin evaporated in vacuo a filtered soln. of lithium carbonate in persulphuric acid; and found that the pink, crystalline product contained about 82 per cent. of lithium persulphate—the remainder was lithium sulphate. The salt of a higher degree of purity was not obtained. R. Löwenherz obtained **sodium persulphate,** $Na_2S_2O_8$, by triturating a conc. soln. of sodium hydroxide or carbonate with solid ammonium persulphate, and he crystallized the salt by adding alcohol or evaporating in vacuo. It was also obtained by triturating solid, hydrated sodium carbonate with solid ammonium persulphate; and also by electrolyzing a soln. of sodium sulphate as positive electrolyte and sulphuric acid as negative electrolyte, and neutralizing the former from time to time with sodium carbonate. H. Marshall found that the great solubility of the sodium salt prevented him making it by the electrolytic process, although the anode liquor contained a soln. of the salt. According to A. Blumer, and the Vereinigte chemische Werke, beneficial results are obtained in the manufacture of sodium persulphate by the addition of simple or complex cyanides—*e.g.* potassium ferrocyanide—in small quantities to the electrolyte. Alkali cyanates, thiocyanates, and cyanamides produce a similar effect. The addition of small quantities of potassium salts causes the sodium persulphate to separate in a granular form, and not as a paste which is purified only with difficulty. R. Löwenherz said that sodium persulphate is very soluble in water, and crystallizes badly. H. Stamm studied its solubility in aq. ammonia.

H. Marshall precipitated **potassium persulphate,** $K_2S_2O_8$, by adding potassium carbonate to a soln. of ammonium persulphate. H. Marshall, C. Diesler, the Konsortium für elektrochemische Industrie, and G. Teichner and P. Askenasy also obtained it by the electrolysis of a sat. soln. of potassium sulphate in sulphuric acid—*vide supra.* The salt is washed with cold water, or recrystallized by rapidly filtering and cooling the hot soln. H. Marshall said that the salt furnishes small prisms, or if slowly cooled, tabular and prismatic crystals, which, according to A. Fock, are triclinic prisms with the axial ratios $a:b:c=0{\cdot}57564:1:0{\cdot}57446$, and $\alpha=81^\circ\ 21'$, $\beta=94^\circ\ 15\frac{1}{2}'$, and $\gamma=91^\circ\ 16'$. Twinning occurs about the (010)-plane. J. Möller found the lowering of the f.p. agrees with the mol. wt. 99 to 108; and H. Marshall's analysis agrees with the formula $K_2S_2O_8$. According to H. Marshall, the salt gives off sulphur trioxide and oxygen when heated. M. Berthelot gave for the heat of formation (2S,8O,2K)=396·3 Cals.; and (2S,8O,2K,Aq.) =381·9 Cals. The heat of soln. is 14·36 Cals. H. Marshall measured the electrical conductivity, and G. Bredig gave for the electrical conductivity, λ, of the aq. soln. for an eq. of the salt in v litres.

v . . .	32	64	128	256	512	1024
λ . . .	118·4	126·3	132·7	137·2	140·7	143·5

H. Marshall said that potassium persulphate is less soluble in water than any other sulphate: 100 parts of water at 0° dissolve 1·77 parts of potassium persulphate. The salt is more soluble in hot water with a slight decomposition. The aq. soln. gradually decomposes in the course of a few months at ordinary temp. and forms the acid sulphate with the evolution of oxygen; the decomposition is faster when the aq. soln. is heated—*vide supra,* ammonium persulphate. D. Vitali found that the salt decomposes in moist air, and by treatment with alcohol. A. Bach observed that with anhydrous sulphuric acid five-eighths of the active oxygen forms a higher per-acid, and three-eighths a simpler per-acid. H. Stamm found that soln. with 0, 1·662, and 3·524 mols of NH_3 per 100 grms. of water dissolve respectively 0·030, 0·022, and 0·026 mols $K_2S_2O_8$. The general reactions have been described previously in connection with persulphuric acid.

A. R. Forster and E. F. Smith prepared **rubidium persulphate,** $Rb_2S_2O_8$, by electrolyzing in a divided cell a soln. consisting of two-thirds sulphuric acid of sp. gr. 1·35, and one-third of a sat. soln. of rubidium sulphate. A white precipitate was slowly deposited at the anode, and it was washed with cold water. The salt crystallized from water in acicular, vitreous forms. They prepared in a similar way **cæsium persulphate,** $Cs_2S_2O_8$, and obtained it in colourless needles. H. Marshall obtained both salts by double decomposition with ammonium persulphate, and recrystallization from aq. soln. He said that the crystals are not isomorphous with those of the potassium salt (triclinic), but with those of the ammonium salt (monoclinic). As mixtures of the potassium salt with the others have been obtained in well-formed monoclinic crystals, notwithstanding a great preponderance of potassium salt, the three salts form an isodimorphous group. A. R. Forster and E. F. Smith said that 100 parts of water dissolve 3·4 parts of rubidium persulphate at 22·5°, and 8·71 to 8·98 parts of cæsium persulphate at 23°.

H. Marshall obtained a very impure **copper persulphate,** CuS_2O_8, by double decomposition between copper sulphate and barium persulphate. During the evaporation of the filtered liquid, decomposition occurred with the formation of a considerable quantity of sulphate, and free acid. If the free sulphuric acid be neutralized from time to time by the addition of some barium carbonate, double decomposition occurs, forming insoluble copper carbonate and soluble barium persulphate. The evaporation of the soln. of the copper salt gave a blue, deliquescent, crystalline solid containing sulphate and persulphate. As in the case of the zinc salt (*q.v.*), G. A. Barbieri and F. Calzolari prepared **copper tetramminopersulphate,** $CuS_2O_8.4NH_3$; and **copper pyridinopersulphate,** $CuS_2O_8.4C_5H_5N$. G. T. Morgan and F. H. Burstall prepared **copper bisethylenediaminopersulphate,** $[Cu\ en_2]S_2O_4$, in purple-red, acicular crystals, by adding potassium persulphate to an aq. soln. of a mol of copper sulphate and 2 mols of ethylenediamine, and washing the product successively with cold water, alcohol, and dry ether. The salt is very unstable, and liable to explode. It is decomposed when left in air in a desiccator leaving a blue residue. The salt detonated on percussion and exploded on heating or on warming with conc. sulphuric acid. Although only very sparingly soluble in cold water, the persulphate dissolves more readily on warming; the purple soln. which changes to blue without appreciable evolution of gas, yields with barium salts a copious precipitate of barium sulphate. Silver nitrate gives no reaction in the cold, but, on warming oxygen is evolved and the purple soln. changes to blue. Conc. hydrochloric acid causes decomposition with evolution of chlorine.

According to H. Marshall, when silver nitrate is treated with potassium persulphate, no immediate precipitate is obtained, but the liquid gradually acquires an inky appearance, and, after some time, a black precipitate of peroxide of silver separates. The liquid at the same time becomes strongly acid. This action is apparently due to the fact that **silver persulphate** is decomposed by water like some other silver salts of acids of sulphur, sulphur trioxide being removed: $Ag_2SO_4+H_2O=Ag_2O+H_2SO_4$. The accumulation of acid seems to stop the action, as the cautious addition of dil. alkali produces a further precipitation. This reaction—noticed before the nature of the salt was known—was at first supposed to be a reducing one, with separation of metallic silver—*vide* silver peroxysulphate, 3. 22, 23. **Silver pyridinoperdisulphate** is formed in golden yellow acicular crystals, $Ag_2S_2O_8.4C_5H_5N$, by adding a soln. containing silver nitrate and pyridine to a cold soln. of potassium perdisulphate. The salt is stable in diffused light; is instantly decomposed by dil. ammonia; and furnishes argentic oxide, AgO, when treated with dil. acids or alkali hydroxide soln.

H. Marshall obtained impure **calcium persulphate,** possibly $CaS_2O_8.nH_2O$, in a very soluble form very difficult to crystallize. A. Kailan examined the action of radium radiations on the salt. A. H. Erdenbrecher obtained calcium persulphate by extraction with alcohol from a dried mixture resulting from the action of calcium oxide on ammonium persulphate. H. Marshall obtained impure **strontium persulphate,** $SrS_2O_8.nH_2O$, as a very soluble salt difficult to crystallize; and **barium persulphate,** $BaS_2O_8.4H_2O$, by triturating a sat., aq. soln. of ammonium persulphate with an excess of barium hydroxide, and passing a current of air over the product to drive off the major portion of the ammonia. The remaining ammonia was removed in vacuo over sulphuric acid. Carbon dioxide was passed through the liquid to remove the excess of barium hydroxide, and any barium hydrocarbonate formed was decomposed by placing the soln. in vacuo for a short time. The filtrate was evaporated in vacuo, and any sulphuric acid formed by the decomposition of the soln. was neutralized from time to time with barium hydroxide. The evaporation is discontinued as soon as crystals begin to form; the crystals are redissolved in the smallest possible amount of water, and the filtered soln. cooled with ice, so that crystallization occurs. The resulting transparent, interlocking, more or less striated, prismatic, probably monoclinic crystals are more pure than those obtained by the gradual evaporation of the aq. soln. The crystals become turbid in a few days owing to the formation of barium sulphate, and they then crumble to form a moist, powdery mass. The crystals are best preserved in a moist atm. 100 parts of water dissolve 52·5 parts of the salt at 0°. The aq. soln. gradually decomposes; and a dil. aq. soln. may remain clear until near the b.p. when it becomes turbid owing to the separation of barium sulphate. The last traces of persulphate are destroyed only by prolonged boiling. If the crystals of the *tetrahydrate* are digested for several days with successive portions of absolute alcohol, the latter removed with anhydrous ether, and the product dried in a current of dry air, the *monohydrate*, $BaS_2O_8.H_2O$, is formed. The salt cannot be dehydrated any further without decomposition: $BaS_2O_8.H_2O = BaSO_4 + H_2SO_4 + O$. M. Berthelot gave for the heat of decomposition $BaS_2O_8aq. + H_2O = BaSO_4 + H_2SO_4 + O + 44{\cdot}2$ Cals.; and for the heat of neutralization, $(H_2S_2O_8, Ba(OH)_2aq.) = 27{\cdot}6$ Cals.

H. Marshall did not succeed in making **magnesium persulphate,** MgS_2O_8, by electrolysis. A white, muddy deposit of dehydrated sulphate was obtained, but no trace of persulphate could be detected. The mother liquor was not much oxidized. G. A. Barbieri and F. Calzolari prepared a complex salt—**magnesium bishexamethylenetetraminopersulphate,** $MgS_2O_4.8H_2O.2C_3H_{12}N_4$. O. Aschan obtained **ammonium magnesium persulphate,** $Mg(NH_4O)_2(SO_2.O)_2.6H_2O$, by the action of magnesium on a cold soln. of ammonium persulphate; with sodium persulphate, **sodium magnesium persulphate,** $Mg(NaO)_2(SO_2.O)_2.4H_2O$, is formed; and with potassium persulphate, **potassium magnesium persulphate,** $Mg(KO)_2(SO_2.O)_2.6H_2O$, is formed. H. Marshall obtained impure **zinc persulphate,** ZnS_2O_8, in soln. by double decomposition between zinc sulphate and barium persulphate in the right proportions. On evaporating the filtered liquid over sulphuric acid in vacuo, a mass of minute needles was obtained. This deliquesced on exposure to air, and contained a large proportion of sulphate mixed with persulphate. The two could not be separated owing to the great solubility of the sulphate, and the continuous decomposition of the persulphate. G. A. Barbieri and F. Calzolari prepared **zinc tetramminopersulphate,** $ZnS_2O_8.4NH_3$, by adding a conc. soln. of 2 mols of ammonium persulphate to a conc., strongly ammoniacal soln. of a mol of zinc sulphate. The crystalline product was washed with ammonia, and dried with bibulous paper. The crystals lose ammonia readily and explode on heating or by percussion. The corresponding **zinc pyridinopersulphate,** $ZnS_2O_8.4C_5N_5H$, was also obtained. O. Aschan prepared by the action of zinc on cold aq. soln. of ammonium, sodium, and potassium persulphates, the corresponding complex salts: **ammonium zinc persulphate,** $Zn(NH_4O)_2(SO_2.O)_2.6H_2O$; **sodium zinc persulphate,** $Zn(NaO)_2(SO_2.O)_2.4H_2O$; and **potassium zinc persulphate,** $Zn(KO)_2(SO_2.O)_2.6H_2O$. They also prepared **cadmium hexamminopersulphate,** $CdS_2O_8.6NH_3$, in a similar way; and likewise **cadmium pyridinopersulphate,** $CdS_2O_8.4C_6H_5N$. O. Aschan obtained **ammonium cadmium persulphate,** $Cd(NH_4O)_2(SO_2.O)_2.6H_2O$; **sodium cadmium persulphate,** $Cd(NaO)_2(SO_2.O)_2.4H_2O$; and **potassium cadmium persulphate,** $Cd(KO)_2(SO_2.O)_2.6H_2O$, as in the case of the corresponding zinc salts.

F. Fichter and S. Stern allowed a mixture of 10 grms. of mercury, 20 grms. of ammonium persulphate, and 50 to 60 c.c. of conc. aq. ammonia to react, and obtained **mercuric tetramminopersulphate,** $[Hg^{\cdot\cdot}(NH_3)_4]S_2O_8$, which loses ammonia in air, but it can be recrystallized from a soln. in conc. aq. ammonia. Mercuric acetate or nitrate, but not the chloride or cyanide, can replace the mercury. The salt is readily hydrolyzed to the mixture of basic salts. N. Tarugi found that mercury or mercurous chloride is readily attacked by an ammoniacal soln. of ammonium persulphate. If the temp. does not exceed 60°, the cooling liquid deposits white, acicular crystals, arranged in radiating agglomerates, of **ammonium mercurous diamminopersulphate,** $HN_4.S_2O_8.Hg.2NH_3$, this substance is insoluble in nitric or sulphuric acid, but dissolves in hydrochloric acid, and colourless guaiacum tincture ; on heating it is decomposed by water, yielding the ammonio-mercurous salt of Caro's acid and ammonium sulphate : $NH_4.S_2O_8.Hg.2NH_3+H_2O = NH_4.SO_5.Hg+(NH_4)_2SO_4$. The addition of water to the mother liquor remaining after the deposition of this compound causes the precipitation of an amorphous, white basic salt of the composition $2NH_4.SO_4.Hg,2NH_3,3Hg_2O$. F. Fichter and S. Stern consider that N. Tarugi's salt is the mercuric tetramminopersulphate.

A. R. Forster and E. F. Smith prepared **thallous persulphate,** probably $Tl_2S_2O_8$, by the method they employed for the rubidium and cæsium salts ; and H. Marshall, by double decomposition of a thallous salt with ammonium persulphate. The impure salt furnishes crystals isomorphous with those of the monoclinic ammonium salt. Thallous persulphate, $Tl'_2S_2O_8$, is isomeric with thallosic sulphate, $Tl'Tl'''(SO_4)_2$ or $Tl_2SO_4.Tl_2(SO_4)_3$.

H. Marshall found that barium persulphate is easy to make because of the insolubility of the sulphate ; lead sulphate is also insoluble, but the oxide and hydroxide are likewise insoluble. This makes the preparation of **lead persulphate** more difficult. If lead oxide be triturated with a sat. soln. of ammonium persulphate much ammonia is evolved, but lead dioxide and no persulphate is formed. He prepared lead persulphate by treating persulphuric acid, in the cold, with lead carbonate. The clear liquid was evaporated in vacuo, and the evaporating soln. was filtered from time to time to remove the lead sulphate. Lead persulphate, like the silver salt, requires the presence of free acid to prevent the deposition of the dioxide. Analysis of the product agrees with either the dihydrate or, more probably, the *trihydrate*, $PbS_2O_8.3H_2O$. The salt is soluble in water ; it deliquesces in a moist atm. ; and a soln. of the salt gives a white precipitate of hydroxide when treated with alkalies. The white precipitate soon forms the dioxide. This salt should not be confused with plumbic sulphate, $Pb(SO_4)_2$—**7.** 47, 30.

H. Marshall showed that a soln. of a manganese salt when warmed with a persulphate gives a precipitate of the dioxide. G. A. Barbieri and F. Calzolari prepared a complex salt of **manganese persulphate** with hexamethylenetetrammine, $MnS_2O_8.8H_2O.2C_6H_{12}N_4$. M. Nakao prepared manganese persulphate by the electrolytic oxidation of manganous sulphate using a soln. in 50 per cent. sulphuric acid at about 50°, and a current density of 5 to 16 amp. per sq. m. When the maximum formation is attained, the proportion of persulphate in the soln. gradually diminishes. Manganese persulphate oxidizes toluene at 50°. H. Marshall found that cobalt salts behave like those of manganese, and G. A. Barbieri and F. Calzolari obtained **cobalt persulphate** as a complex salt—**manganese bishexamethylenetetraminopersulphate,** $CoS_2O_8.8H_2O.2C_6H_{12}N_4$. O. Aschan prepared by the process employed for the corresponding zinc salts : **ammonium ferrous persulphate,** $Fe(NH_4O)_2(SO_2.O).6H_2O$; **sodium ferrous persulphate,** $Fe(NaO)_2(SO_2.O)_2.4H_2O$; and **potassium ferrous persulphate,** $Fe(KO)_2(SO_2.O)_2.6H_2O$. Likewise also with **ammonium cobalt persulphate,** $Co(NH_4O)(SO_2.O)_2.6H_2O$; **sodium cobalt persulphate,** $Co(NaO)_2(SO_2.O)_2.4H_2O$; and **potassium cobalt persulphate,** $Co(KO)(SO_2.O)_2.6H_2O$. S. M. Jörgensen obtained **cobalt hexamminodisulphatopersulphate,** $[Co(NH_3)_6]_2(SO_4)_2(S_2O_8)$, in yellow rhombic plates, by the interaction of an ammoniacal soln. of cobalt sulphate and ammonium persulphate under press. H. Marshall found that nickel salts behave like cobalt salts, but the dioxide is precipitated only in the presence of an alkali. G. A. Barbieri and F. Calzolari obtained a complex salt—**nickel bishexamethylenetetraminopersulphate,** $NiS_2O_8.8H_2O.2C_6H_{12}N_4$; as well as **nickel pyridinopersulphate,** $NiS_2O_8.4C_5H_5N$; while **nickel hexamminopersulphate,** $NiS_2O_8.6NH_3$, was obtained as in the case of the zinc salt. O. Aschan prepared the following salts by the process employed for the corresponding zinc salts : **ammonium nickel persulphate,**

$Ni(NH_4O)_2(SO_2.O)_2.6H_2O$; **sodium nickel persulphate,** $Ni(NaO)_2(SO_2.O)_2.4H_2O$; and **potassium nickel persulphate,** $Ni(KO)_2(SO_2.O)_2.6H_2O$.

A. Villiers prepared what he regarded as **sodium disulphopersulphate,** $Na_2S_4O_8$. Sodium thiosulphate was mixed with an insufficient quantity of water for soln., and the mixture sat. with sulphur dioxide ; if any salt remained undissolved more water was added, and the mixture was again saturated with the gas. A yellow soln. was obtained, and if this be evaporated immediately in vacuo, it evolves sulphur dioxide, and, if the temp. does not exceed 0°, only sodium thiosulphate is obtained from the residue. If the soln. be allowed to remain at the ordinary temp. for two or three days, it will then absorb more sulphur dioxide, and if, after saturation, it is allowed to remain for a day or two and then evaporated in vacuo over sulphuric acid, it yields brilliant, white, brittle, anhydrous prisms of the anhydrous salt. The evaporation of the aq. soln. at a low temp. furnishes the dihydrate, $Na_2S_4O_8.2H_2O$, in soft, waxy crystals arranged in nodules. If any trithionate be present, the mixed crystals are exposed to air. The trithionate effloresces and the unaltered crystals of the dithiopersulphate are easily picked out. Tetrathionate is produced in addition to the other two salts, and it is possible that the reactions take place in accordance with the equations: $2Na_2S_2O_3+3SO_2=Na_2S_4O_6+Na_2S_3O_6$, and $2Na_2S_2O_3+4SO_2=Na_2S_4O_6+Na_2S_4O_8$. Anhydrous sodium disulphopersulphate furnishes rhombic prisms which do not alter when exposed to air, but melt at 125°, and intumesce at 140° giving off sulphur dioxide, and leaving a residue which contains a sulphate and free sulphur, but no alkaline sulphide. The hydrated salt decomposes slowly in the cold and rapidly when heated, with evolution of sulphurous anhydride and formation of the trithionate. Sulphur dioxide has no action on the trithionate at the ordinary temp. The disulphopersulphate does not reduce potassium permanganate even when heated, but is converted into sulphate by the action of bromine, five equivalents of bromine being required for each equivalent of the salt. Its soln. gives no precipitation with metallic salts except mercuric chloride, which produces a precipitate of sulphur. When boiled with cupric sulphate, there is no precipitation of cuprous sulphide as with the trithionate, except after prolonged ebullition ; conc. mineral acids seem to liberate **dithiopersulphuric acid** from its salts without decomposing it. Nitric acid above a certain strength, however, oxidizes it rapidly, and even explosively, with precipitation of sulphur and evolution of nitrogen oxides. A. Villiers afterwards showed that his disulphopersulphate was probably a tetrathionate, $Na_2S_4O_6.2H_2O$; but E. J. Maumené held that the disulphopersulphate really exists, and he called the anhydride, S_4O_7, corresponding acid $H_2S_4O_8$, *l'acide tetrasulfugique*—the " g " was introduced because it is the seventh letter of the alphabet.

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§ 36. Permonosulphuric Acid, and the Permonosulphates

As indicated in connection with perdisulphuric acid, M. Traube's[1] anomalous results with persulphuric acid prepared by electrolysis were explained when N. Caro observed that at least two different persulphuric acids were involved. Under the influence of conc. sulphuric acid the perdisulphuric acid forms a variety which, unlike perdisulphuric acid, does not yield aniline-black when treated with aniline; and which instantly liberates iodine from acidic soln. of potassium iodide, whereas the reaction with the perdisulphuric acid is comparatively slow. A. von Bäyer and V. Villiger showed that the formula for **Caro's acid** is H_2SO_5—**permonosulphuric acid.** They also showed that the product of the action of conc. hydrogen dioxide on sulphuric acid contains permonosulphuric acid, and not, as supposed by M. Berthelot, perdisulphuric acid. H. Ahrle attempted to make permonosulphuric acid from anhydrous hydrogen dioxide and either sulphuric acid or sulphur trioxide, but the results were not very satisfactory. He measured the equilibrium constant of the reaction $H_2SO_4+H_2O_2 \rightleftharpoons H_2SO_5+H_2O$, and found that K in $[H_2SO_4][H_2O_2]=K[H_2SO_5][H_2O]$ is about one-third—on the assumption that the permanganate titration is an accurate means of determining hydrogen dioxide in the presence of permonosulphuric acid. N. Caro, and T. S. Price, and J. A. N. Friend prepared permonosulphuric acid as follows:

Ten grams of potassium perdisulphate were triturated at a low temp. with 20 grms. of conc. sulphuric acid, and the mixture allowed to stand for an hour—if a longer time is occupied, the mixture begins to decompose—and it is then diluted by pouring it on to crushed ice. The sulphuric acid was then precipitated by the addition of freshly prepared barium hydrophosphate—barium carbonate or hydroxide decomposes the acid—and the liquid filtered through porous earthenware. The filtrate was then treated with a current of air under reduced pressure until it no longer smelt of ozone. It contained about 16 per cent. of the permonosulphuric acid, but no hydrogen dioxide; and only a trace of barium sulphate.

R. H. Vallance prepared soln. of permonosulphuric acid as follows:

A porcelain dish containing 20 grms. of powdered potassium perdisulphate was embedded in a freezing mixture, and the salt triturated with 13 c.c. of concentrated sulphuric acid, the operation occupying about 15 minutes. The mixture was kept for 50 minutes, after which it was diluted by pouring on to 50 grms. of freshly made ice contained in a beaker deeply immersed in a freezing mixture. It was then neutralized by slowly adding a soln. of potassium carbonate (equivalent to the amount of sulphuric acid taken) in the smallest quantity of water, fresh lumps of ice being added when necessary. This operation occupied about 30 minutes, and the final neutralization was effected by the addition of a little anhydrous potassium carbonate. The mixture was filtered and concentrated in vacuo over sulphuric acid, until the vol. was about 50 c.c.

The relation of permonosulphuric acid to the other persulphuric acids was investigated by T. S. Price, T. M. Lowry and J. H. West, H. E. Armstrong, etc. This work has been discussed in what precedes. The general conclusion is that there is a progressive hydrolysis: $H_2S_2O_8+H_2O=H_2SO_4+H_2SO_5$; and $H_2SO_5+H_2O=H_2SO_4+H_2O_2$. T. S. Price prepared an impure potassium permonosulphate $KHSO_5$, as follows:

A soln. of permonosulphuric acid was prepared by the action of 25 c.c. of conc. sulphuric acid on 25 grms. of potassium perdisulphate as indicated by T. S. Price, and J. A. N. Friend. The soln. was diluted and neutralized at the same time by being run very slowly into a soln. of potassium carbonate (containing enough carbonate to neutralize the sulphuric acid taken), in which was ice freshly made from distilled water. The temp. of the aq. soln. of potassium carbonate, which was −7° before the soln. of permonosulphuric acid was run in, gradually rose to about 0° during the process of dilution. The potassium sulphate which separated out was filtered off, the mother liquor being drained away as completely as possible. The filtrate generally contained an amount of persulphuric oxygen which was eq. to about 18 grms. of H_2SO_5 per litre. If the mixture containing the acid was first diluted by being poured on to broken ice, and then neutralized with potassium carbonate, the filtrate was only about half the above strength. The filtrate was generally acid, and was neutralized by the further addition of anhydrous potassium carbonate, which was added carefully until no further effervescence took place. Potassium sulphate was separated from the neutral soln. by freezing, and the soln. evaporated to dryness in a vacuum desiccator over conc. sulphuric acid. The process of evaporation lasted between a week and a fortnight, and the potassium sulphate, which separated out continuously, was filtered off from time to time until the soln. became so concentrated that it could not be filtered without undergoing appreciable loss; it was then allowed to evaporate to dryness. During the evaporation of the soln., the conc. of the permonosulphate continually increases, but at the same time some of the salt decomposes with the formation of potassium hydrogen sulphate. This is the reason why it is immaterial whether the neutralization with potassium carbonate be exact or not. The mixture so obtained was powdered as finely as possible, and finally dried in a vacuum desiccator. The permonosulphate contained potassium sulphate, hydrosulphate, perdisulphate as impurities.

Permonosulphuric acid was obtained by the Badische Anilin- und Sodafabrik, T. S. Price, J. A. N. Friend, A. von Baeyer and V. Villiger, M. Mugdan, and N. Caro, by the action of sulphuric acid on persulphates or persulphuric acid, as indicated above; it was also obtained by the Badische Anilin- und Sodafabrik, A. von Baeyer and V. Villiger, and K. Elbs and O. Schönherr by the electrolysis of conc. sulphuric acid, for the primary perdisulphuric acid (*q.v.*) is hydrolyzed by sulphuric acid of the right concentration. C. Tubandt and W. Riedel said that when freshly precipitated nickel dioxide is treated either with dil. or conc. sulphuric acid, or with conc. potassium hydrosulphate, a soln. containing permonosulphuric acid is formed. J. d'Ans and W. Friederich synthesized the pure, anhydrous acid by gradually adding the theoretical proportion of 100 per cent. hydrogen dioxide to pure, well-cooled chlorosulphonic acid: $ClHSO_3+H_2O_2=HCl+H_2SO_5$. When the evolution of hydrogen chloride has ceased, the mass was allowed to warm up slowly, and the hydrogen chloride pumped off. The frozen mass was purified by centrifuging, and subsequent fusion, and recrystallization.

The properties of permonosulphuric acid.—The anhydrous acid prepared by J. d'Ans and W. Friederich is a white crystalline solid which melts at 45° with slight decomposition. It can be kept for several days as a solid, but gradually loses ozonized oxygen. When moist it decomposes rapidly, and some perdisulphuric acid is formed at the same time. Thus a 97 per cent. acid, after 8 days, contained 82·7 per cent. H_2SO_5 and 15·3 per cent. $H_2S_2O_8$. It reacts like anhydrous perdisulphuric acid, but not so vigorously. Even when the anhydrous acid is dissolved in ice-cold water, it undergoes slight decomposition, $H_2SO_5+H_2O\rightleftharpoons H_2O_2+H_2SO_4$. A cryoscopic determination of the mol. wt. in aq. soln. agrees with the assumption that the acid is completely ionized $H_2SO_5\rightleftharpoons H^{\cdot}+HSO_5'$. According to A. von Baeyer and V. Villiger, the aq. soln. is fairly stable in the presence of 8 per cent. sulphuric or phosphoric acid. T. S. Price found that 10 c.c. of the acid, eq. to 27·7 c.c. of thiosulphate, was, after 84 days, eq. to 27·1 c.c., and after 29 days more, to 26·8 c.c. A. von Baeyer and V. Villiger said that the soln. generally has a strong odour resembling bleaching powder—due, they said, to the presence of volatile S_2O_8—according to E. Bamberger, and H. Ahrle, the odour resembles ozone. In acidic soln., permonosulphuric acid is more stable than perdisulphuric acid, but in neutral or alkaline soln., less stable. R. Willstätter and E. Hauenstein observed that the alkaline soln. readily decomposes, but it is more stable in the presence of a large excess of potassium hydroxide. E. Bamberger said that the acid neutralized by potassium carbonate is decomposed when warmed with a catalyst—say platinum sponge—and ozone is evolved. H. Ahrle said that the decomposition of conc.—92 per cent.—soln. is rapid at the body temp.; and that the decomposition is explosive in the presence of smooth or finely-divided platinum, manganese dioxide, or silver. The action is not violent with zinc dust, lead dust, magnesium powder, or wood charcoal; and the soln. is not decomposed by finely divided iron. T. S. Price, and J. A. N. Friend showed that a dil. soln. of the acid decomposes very slowly in the presence of colloidal platinum, but if **hydrogen dioxide** be present there is a rapid evolution of oxygen, probably due to the reaction $H_2SO_5+H_2O_2=H_2SO_4+H_2O+O_2$, which is accelerated by the platinum. The Konsortium für elektrochemische Industrie, K. Anders, O. Urbasch, Oesterreichische chemische Werke and L. Löwenstein, and H. Teichner prepared hydrogen dioxide from the hydrolyzed permonosulphuric acid.

The reactions of permonosulphuric acid closely resemble those of perdisulphuric acid. E. Wedekind showed that **hydrofluoric acid** is not attacked by permonosulphuric acid, and attempts to prepare fluorine by the action of the acid on **hydrogen fluoride** gave negative results. The acid liberates chlorine from **hydrochloric acid** or **hydrogen chloride** and bromine from **hydrogen bromide.** As previously indicated, the acid liberates iodine immediately from **potassium iodide,** while the action with perdisulphuric acid is slow, and very slow with hydrogen dioxide and dil. sulphuric acid.

According to N. Caro, and the Badische Anilin- und Sodafabrik, permonosulphuric acid oxidizes the amido-group of the **primary amines** to nitroso- and nitro-groups ; **aniline** is instantly oxidized to nitrobenzol, and, as indicated above, aniline black is not formed. E. Bamberger, E. Seel, R. Wolffenstein, N. Tarugi, C. F. Cross and co-workers, M. Dittrich, W. Migault, F. Erben, H. Ditz, E. Springer, A. A. Albitzky, R. Fosse and P. Bertrand, and A. von Baeyer and V. Villiger studied the oxidation of **organic compounds** by permonosulphuric acid. H. Ahrle found that the 92 per cent. acid carbonizes **wool,** and **cellulose** very quickly, while with **cotton** there is at first no action, but in a few seconds there is a violent action accompanied by a yellow flame. A. von Baeyer and V. Villiger said that **titanium salts** are not coloured yellow by permonosulphuric acid, although A. Bach said that the undiluted soln. made from 100 per cent. sulphuric acid and potassium perdisulphate does give a yellow colour—presumably because some hydrogen dioxide was present, although A. Bach said that it was not so.

According to T. S. Price, soln. of permonosulphuric acid cannot be satisfactorily titrated with **potassium hydroxide** soln. using phenolphthalein or methyl-orange as indicators—the latter indicator is rapidly oxidized, and with phenolphthalein, the indication is not sharp—owing, it is suggested, to the slight acidity of the HO.O-group. A. von Baeyer and V. Villiger said that the acid is decomposed by **barium hydroxide,** but not by **barium phosphate.** N. Tarugi found that ammonium mercurous diamminopersulphate (*q.v.*) is decomposed by water, forming **ammonium mercurous permonosulphate,** $NH_4.SO_5.Hg$. E. Bamberger found that a neutralized soln. of permonosulphuric acid froths violently when treated with **silver nitrate,** and a similar reaction is produced with **manganese and lead dioxides.** An ozonized gas is evolved. On adding a **copper salt** and then sodium hydroxide to a soln. of permonosulphuric acid, a brownish-black precipitate of copper peroxide is formed which soon decomposes with the evolution of oxygen. This precipitate has a different appearance from that produced by hydrogen dioxide under similar conditions.

A. von Baeyer and V. Villiger [2] found that a mixture of potassium permanganate, permonosulphuric acid, and dil. sulphuric acid is a very strong oxidizing agent. Permonosulphuric acid free from hydrogen peroxide does not act on an acidic soln. of **potassium permanganate,** for, after standing several hours, no reaction can be perceived. On the other hand, if a little manganese sulphate be present, there is a slow reaction, the permanganate is reduced, and the permonosulphuric acid is decomposed ; a higher manganese oxide is soon deposited, and the evolution of gas becomes more marked. The liquid acquires a red colour not due to permanganate. Manganese sulphate alone does not decompose the acid. In titrating hydrogen dioxide in the presence of permonosulphuric acid, by means of potassium permanganate soln., a little manganese sulphate is added. T. S. Price showed that the method is inaccurate. The longer the time occupied by the titration, the lower the results. This is attributed to the induced reaction between the hydrogen dioxide and the permonosulphuric acid, and to the catalytic effect of this reaction on some manganese compound formed in the soln. This explains how the amount of oxygen evolved, when a soln. containing hydrogen dioxide and monopersulphuric acid is titrated with permanganate, is always in excess of that calculated from the permanganate used. This result was observed by A. Bach, and M. Berthelot, and gave rise to a discussion between A. Bach, H. E. Armstrong, W. Ramsay, etc.—*vide supra.*

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§ 37. Thiosulphuric Acid

In 1799, F. Chaussier[1] obtained a by-product in the preparation of sodium carbonate by reducing sodium sulphate with coal ; and also by the action of sodium sulphide or hydrogen sulphide on sulphurous acid. He called the product *hydrosulfure sulfuré de soude.* Next year, L. N. Vauquelin regarded it as a compound of sodium sulphite and sulphur, and obtained it by boiling sodium sulphite with sulphur, and called it *sulfite sulfuré de soude,* so that the acid would be *sulphosulphurous acid.* In 1803, C. L. Berthollet suggested that the salt is a compound of sodium sulphite with hydrogen sulphide and not sulphur. L. N. Vauquelin's view was accepted until about 1813, when J. L. Gay Lussac inferred that this same salt is really a derivative of an acid less oxidized than sulphurous acid, and he accordingly called it *hyposulfite de soude* –hyposulphite of soda. This term was accepted by J. F. W. Herschel and was in general use until 1877 when R. von Wagner proposed to call the acid *Thioschwefelsäure*—**thiosulphuric acid**—in order to emphasize its relationship to sulphuric acid, and at the same time prevent confusion with P. Schützenberger's *l'acide hydrosulfureux,* which is really a less oxidized acid than sulphurous acid. R. von Wagner's proposal has been accepted by the majority of chemists, although the older designation persists in the photographer's *hyposulphite of soda,* or *hypo,* which is really the salt now called sodium thiosulphate.

E. Willm[2] observed in the hot sulphuretted waters of Olette, Pyrénées Orientales, 0·0057 to 0·0096 per cent. of sulphur as sulphides, 0·0098 to 0·0113 per cent. as thiosulphate ; and 0·0168 to 0·0360 per cent. as sulphuric acid. S. Dezani discussed the occurrence of thiosulphates in urine. E. Salkowsky found that the urine of rabbits fed on white cabbage contains a considerable amount of thiosulphate. Observations were also made by A. Strümpell, and A. Heffter. The occurrence of thiosulphates in the residue after the explosion of gunpowder was discussed by A. Noble and F. A. Abel, and M. Berthelot. G. Guittonneau found that with sulphur in a culture medium, various soil organisms oxidized sulphur to sulphate with the formation of some thiosulphate which was supposed to represent an intermediate stage in the oxidation. The conversion to sulphate is inhibited in the presence of ammonium succinate so that thiosulphate accumulates in the system.

The free acid is very unstable and has been prepared only in soln., so that many have doubted whether it has been obtained at all. H. Rose [3] said that he obtained a dil. soln. of the acid which he kept for five months by treating with sulphurous acid an intimate mixture of finely divided cadmium sulphide and sulphur moistened with alcohol. The filtrate freed from the excess of sulphur dioxide was treated with hydrogen sulphide, and the cadmium sulphide filtered off. It is not clear whether the liquid really contained thiosulphuric acid, or a polythionic acid of H. Debus. F. A. Flückiger also supposed thiosulphuric acid to have been made by the action of sulphurous acid on sulphur at ordinary temp., or in a sealed tube at 80° to 90°. A. Debus, and A. Colefax regarded the product as a polythionic acid. J. Aloy said that an alcoholic soln. of thiosulphuric acid is formed by saturating with sulphur dioxide 95 per cent. alcohol holding sulphur in suspension. J. Myers passed water vapour over boiling sulphur and said that both hydrogen sulphide and thiosulphuric acid are formed. F. A. Flückiger said that when roll sulphur, or sulphur crystallized from carbon disulphide, is washed with water, a little thiosulphuric acid will be found in the wash-water. J. Pelouze, and J. Persoz treated lead thiosulphate at 0° with hydrogen sulphide or dil. sulphuric acid, and obtained thiosulphuric acid which rapidly decomposed into sulphur and sulphurous acid. An excess of hydrogen sulphide would convert the liberated thiosulphuric acid into a polythionate. J. L. Gay Lussac also said that when strontium thiosulphate is decomposed by hydrochloric acid, or alcohol sat. with hydrogen chloride, the acid which is set free is quickly resolved into sulphurous acid and sulphur. The action of acids on the thiosulphates was discussed by G. E. M. Foussereau, E. Mathieu-Plessy, M. Berthelot, W. Vaubel, A. Colson, G. Aarland, W. Vaubel, G. Vortmann, A. Seyewetz and G. Chicandard, A. Colefax, etc. F. Muck reported that trithionate (*q.v.*) is formed by boiling a soln. of ammonium sulphate with manganese sulphide, but H. Bassett and R. G. Durrant found that the product is really thiosulphate probably formed by the atm. oxidation of hydrogen (or ammonium) sulphide, a reaction probably catalyzed by manganese oxide. The atm. oxidation of ammonium sulphide yields thiosulphate—*e.g.* an old soln. of ammonium sulphide which had lost its colour and deposited sulphur contained much thiosulphate.

When a thiosulphate is mixed with an acid, the liquid remains clear for a little while, and then becomes turbid, owing to the separation of sulphur. The phenomenon is due to the thiosulphuric acid first formed decomposing after a few minutes: $H_2S_2O_3=H_2SO_3+S$. J. F. W. Herschel stated that when an aq. soln. of an alkali thiosulphate is decomposed by a stronger acid, the liquid acquires a harsh, sour, and very bitter taste, and the property of precipitating metal sulphides from soln. of mercurous or silver nitrate; it exerts no immediate action on salts of copper, zinc, or iron, but in a few seconds, especially if heat be applied, half the sulphur is precipitated, and the other half remains in soln. as sulphurous acid. J. A. Muller observed that, at 12°, when a mol of hydrochloric acid, dissolved in 16 litres of water, is added to a mol of sodium thiosulphate, dissolved in a similar quantity of water, sulphur begins to be deposited after 1·5 minutes, and the reaction continues until one atom of the sulphur is liberated. When 2 mols of hydrochloric acid are employed in the place of 1 mol in such an experiment the precipitation of sulphur is never complete, indicating that, whilst the sodium hydrothiosulphate formed in the first case decomposes completely into sodium hydrosulphite and sulphur, the thiosulphuric acid liberated in the second case is only partially decomposed, yielding sulphurous acid and sulphur. C. Bongiovanni showed that when an aq. alcoholic soln. of methylene blue is added to an acidified soln. of a thiosulphate it is decolorized; sulphurous acid does not affect this reduction, which is taken to indicate that free thiosulphuric acid is really present in soln. J. Scheffer and F. Böhm observed that in the acidified soln. pentathionic acid can be recognized before the turbidity appears. Thiosulphates are not decomposed by acids of smaller ion conc. than $2{\cdot}5\times10^{-5}$. They suppose that the condition necessary for the decomposition of thiosulphuric acid is the presence of the labile ions HS_2O_3', whilst the S_2O_3''-ions and $H_2S_2O_3$ are considered to be stable. Methylene blue is decolorized by thiosulphate soln. even before acidification; if the dye be added 3 hrs. after acidification, it is only partially decolorized. Some methylene blue is adsorbed by the sulphur; but the presence of sulphur dioxide prevents the adsorption. J. C. Gil and J. Beato said that if a conc. soln. of sodium thiosulphate (3 or 4 drops) be added to fuming hydrochloric acid (3 to 4 c.c.), sodium chloride is precipitated, after which the clear soln. can be preserved without change for about an hour at 15°; it gives the reactions typical of thiosulphuric acid. An alcoholic soln. of thiosulphuric acid is obtained by the action of dry hydrogen sulphide on lead thiosulphate (dried at 105°) suspended in alcohol. The precipitated lead sulphide is filtered and excess of hydrogen sulphide removed from the filtrate by a current of air. The acid decomposes in the course of a few days at about 28° into sulphur and, apparently, pentathionic acid.

According to W. Spring and A. Lévy, the acidified soln. of the thiosulphate decomposes into trithionate and hydrogen sulphide, and if sufficient hydrogen sulphide be present the reaction can be arrested; the thiosulphuric acid decomposes: $H_2S_2O_3=H_2SO_3+S$; the sulphur dioxide then reacts with the hydrogen sulphide, forming sulphur and trithionate. A. F. Hollemann said that this explanation is unsatisfactory because no hydrogen sulphide can be detected in the liquid; the decomposition can occur in the presence of a lead salt without the formation of a trace of lead sulphide. H. Debus, and G. Chancel and E. Diacon added that most of the thiosulphuric acid decomposes into sulphur, sulphur dioxide, and water, while a small proportion condenses to pentathionic acid: $5H_2S_2O_3=3H_2O+2H_2S_5O_6$. W. Vaubel found that with formic, acetic, succinic, citric, hydrobromic, hydriodic, hydrofluoric, nitric, sulphurous, dithionic, phosphoric, and very dil. sulphuric acids, the proportions of sulphur and sulphur dioxide formed agree with the equation: $Na_2S_2O_3+2CH_3COOH=2CH_3COONa+H_2O+SO_2+S$. With sulphuric acid of increasing concentration, in the cold, the proportion of sulphur dioxide varied from 74 per cent. of the theoretical with 20 per cent. sulphuric acid to 45·4 per cent. with 100 per cent. sulphuric acid, at the same time the sulphur ranged from the theoretical proportion to 9·15 per cent. of that value, and with the conc. acid, the evolution of hydrogen sulphide was noticed. With 10 to 40 per cent. hydrochloric acid, the sulphur dioxide varied between 82 and 88 per cent. of the theoretical, and the sulphur between 86 and 97 per cent.; while quantities of sulphuric acid corresponding with 6 to 8·5 per cent. of sulphur were formed. W. Vaubel suggested that the first phase of the reaction is a decomposition into hydrogen sulphide and sulphur trioxide: $H_2S_2O_3=H_2S+SO_3$, followed by $H_2S+SO_3=SO_2+S+H_2O$; $2H_2S+SO_2=3S+2H_2O$; and $3H_2S+SO_3=4S+3H_2O$. In support of these equations he quoted the observations of A. Geuther that silver oxide reacts with sodium thiosulphate, forming the calculated quantity of sodium sulphate and silver sulphide; and the observations of A. L. Orlowsky that sodium ethyl thiosulphate is decomposed by acids, forming sulphuric acid and ethyl hydrosulphide. K. Jablczynsky and Z. Rytel showed by spectroscopic observations that the free thiosulphuric acid, in acidified soln. of sodium thiosulphate, immediately decomposes with the formation of sulphurous acid and monatomic sulphur. This reaction is unimolecular and reversible, being retarded by liberated monatomic sulphur and by sulphur dioxide. The sulphur is at first invisible, the solutions becoming opalescent only on the formation of polyatomic aggregates, which then adsorb atomic sulphur from the solution. These aggregates may thus be considered to act as an autocatalyst, since by removing atomic sulphur they accelerate the reaction. According to F. Förster, on mixing soln. containing respectively a mol of hydrosulphide and 2 mols of sulphurous acid, thiosulphate is formed immediately, and almost in theoretical quantities: $2HS'+4HSO_3' \rightarrow 3S_2O_3'+3H_2O$; free sulphur and sulphite ion result as by-products in equimolecular quantities. An excess of sulphurous acid causes the formation of trithionate and sulphite in addition to thiosulphate, but the primary reaction is so rapid that the secondary effects may be observed only if the hydrosulphide soln. be added to the hydrogen sulphite soln.; if the procedure be reversed the excess of sulphurous acid remains unchanged. The reactions are explained on the assumption that a hypothetical sulphur monoxide is concerned in the process. The aq. soln. is supposed to contain, in equilibrium, $H_2SO_2 \rightleftharpoons SO+H_2O$, and it is supposed that in the formation of the thiosulphate, $SO+H_2S=2S+H_2O$; followed by $2SO+H_2O \rightleftharpoons S_2O_3+2H^{\cdot}$—*vide infra*, polythionic acids.

E. H. Riesenfeld and co-workers represented the primary decomposition of thiosulphuric acid by the equation $H_2S_2O_3=H_2SO_3+S$. The appearance of pentathionic acid is due to the reactivity of the freshly-formed colloidal sulphur, $5S+5SO_2+2H_2O=2H_2S_5O_6$, the pentathionic acid reacting with sulphurous acid to form some trithionic acid and more thiosulphuric acid, $S_5O_6+2SO_3=S_3O_6+2S_2O_3$. Trithionic acid slowly decomposes to give a mixture of thiosulphuric and sulphuric acids, $S_3O_6''+H_2O=SO_4''+S_2O_3''+2H^{\cdot}$. G. Vortmann objected that the prolonged contact of the products in W. Vaubel's experiments favoured secondary reaction; by working more quickly in a stream of hydrogen or carbon dioxide so as to remove the sulphur dioxide, the results favoured the view that the first stage of the reaction is in accord with $2H_2S_2O_3=2H_2S+O_2+2SO_2$. In those cases in which metals are present which do not form insoluble sulphides, the oxygen partially oxidizes the hydrogen sulphide with the separation of sulphur, and the sulphur dioxide is set free, whilst in those cases in which the metal present yields a sulphide insoluble in dil. acids, a precipitate of the sulphide is formed, and the oxygen reacts either with the sulphur dioxide, with the formation of sulphuric acid, or with a portion of the undecomposed sodium thiosulphate with the production of tetrathionate or pentathionate; the last reaction, however, ensues only in those cases in which either an excess of thiosulphate is present, or the metallic salt undergoes reduction from a higher to a lower state of oxidation. Sodium thiosulphate reacts with dil. hydrochloric acid in accord with $Na_2S_2O_3+2HCl=2NaCl+S+SO_2+H_2O$. When dil. soln. of the thiosulphate are employed, a small quantity of hydrogen sulphide escapes, but with conc. soln. no noticeable amount is obtained, since the small quantity evolved is decomposed by the sulphur dioxide with the separation of sulphur, which collects on the sides of the flask above the liquid. In addition to the sulphur and sulphur dioxide, tetrathionic acid is formed in quantity corresponding with that obtainable from 20 per cent. of the thiosulphate employed, and traces of pentathionic acid are present, but no evidence could be obtained of the presence of sulphuric acid in the decomposition product. The formation of pentathionic acid is not mentioned by W. Vaubel. The reaction is slightly modified when certain salts of the alkalies or alkaline earths are present; thus, in the presence of potassium iodide, the quantity of liberated sulphur is increased and small amounts of sulphuric acid are formed. In addition to the decomposition of thiosulphuric acid by reversible reaction: $H_2S_2O_3 \rightleftharpoons H_2SO_3+S$, W. Spring and A. Lévy, and A. Colson observed that some hydrogen sulphide is produced, and A. Colson found that the ratio $H_2SO_4 : H_2S$ is variable, and supposed the hydrogen sulphide is a product of the action of nascent sulphur on water. F. Förster and co-workers supposed that the hydrogen sulphide is a minor by-product of a side-reaction: $H_2S_2O_3+H_2O \rightleftharpoons H_2SO_4+H_2S$. E. Schulek attributed the presence of hydrogen sulphide in a standard thiosulphate soln. to bacterial action.

H. Bassett and R. G. Durrant found that hydrogen sulphide is always produced when acids or even water alone acts upon sodium thiosulphate. The gas is evolved if carbon dioxide is bubbled through, or if the thiosulphate is warmed with boric acid, whilst stronger acids liberate it readily. Little or no sulphuric acid is produced unless the mixture is boiled for a long time. It then results from the hydrolysis of tri- and tetra-thionic acids. They stated that hydrogen sulphide is produced by the reversible reaction : $2H_2S_2O_3 \rightleftharpoons H_2S+H_2S_3O_6$; and doubted its production by the reaction assumed by F. Förster and co-workers, because if the reaction is valid, there will be a small increase in the acidity of the soln., and the reaction will be favoured by alkalies and hindered by acids, whilst the formation of thiosulphate from sulphate and sulphide should be favoured by acids. There is no evidence of this, or of any such relation between sulphate and sulphide as is assumed by the supposed reaction. The reaction usually symbolized $Ag_2S_2O_3+H_2O=Ag_2S+H_2SO_4$ can be symbolized, perhaps more satisfactorily, by $2Ag_2S_2O_3=Ag_2S+Ag_2S_3O_6$; followed by $Ag_2S_3O_6+2H_2O=Ag_2S+2H_2SO_4$. J. Fogh found that lead thiosulphate, when heated with water, yields sulphide and trithionate, and, according to H. Bassett and R. G. Durrant, along with some sulphate and sulphur dioxide formed by the decomposition of the trithionate. W. Spring observed the formation of a trithionate and sulphide when a soln. of a complex alkali and silver, mercury, or lead thiosulphate is boiled. Conversely, lead sulphide and potassium trithionate soln. yields lead thiosulphate ; and when lead thiosulphate is boiled with an eq. amount of alkali, or with dil. acetic acid, the thiosulphate is largely converted into trithionate. H. Bassett and R. G. Durrant observed that boiling dil. alkali soln. of sodium thiosulphate yield trithionate and sulphide with only a trace of sulphate —a conc. soln. of alkali favours the formation of thiosulphate ; and boiling the thiosulphate with sodium plumbite yields a precipitate of lead sulphide and a soln. of sodium trithionate. Again, barium thiosulphate decomposes very slowly when boiled with water, a considerable proportion of polythionate is formed, but very little sulphate. The formation of barium sulphate eq. to the barium thiosulphate would be expected if thiosulphuric acid decomposed according to the scheme $H_2S_2O_3+H_2O=H_2SO_4+H_2S$, in which case, moreover, the decomposition should be greatly accelerated by the presence of barium, as it is by the presence of salts of copper, silver, and mercury, even after allowance has been made for the fact that barium sulphate is not nearly so insoluble as the sulphides of these metals.

G. Chancel and E. Diacon showed that polythionic acids are formed by the action of acids on thiosulphates. F. Förster and R. Vogel inferred that pentathionic acid is the primary polythionic acid, because the observed proportions of thiosulphate and sulphite in the soln. fit the equation $5Na_2S_2O_3+6H_2SO_3=2Na_2S_5O_6+6NaHSO_3+3H_2O$ better than $Na_2S_2O_3+4H_2SO_3=Na_2S_3O_6+H_2S_3O_6+3H_2O$. If, as H. Bassett and R. G. Durrant suppose, the trithionic acid is a primary product of the reaction : $2H_2S_2O_3 \rightleftharpoons H_2S+H_2S_3O_6$, the trithionic acid combines with the sulphur formed by the concurrent reactions : $H_2S_2O_3=H_2SO_3+S$, etc., to yield tetrathionic acid : $H_2S_3O_6+S \rightleftharpoons H_2S_4O_6$, and pentathionic acid : $H_2S_4O_6+S=H_2S_5O_6$. This explains the greater consumption of thiosulphate than sulphite observed by F. Förster and R. Vogel. W. Spring and A. Lévy also assume that polythionates are formed from the trithionate produced as just indicated, and G. Chancel and E. Diacon observed the reverse change—the formation of thiosulphate from trithionate and sulphide. According to G. Aarland, the decomposition of thiosulphuric acid, liberated by adding an acid to a thiosulphate, is a reversible process which is hindered when the products of the reaction are present. For example, if a soln. of sulphurous acid be added to a soln. of sodium thiosulphate, no decomposition of the liberated thiosulphuric acid occurs although the mixture is strongly acid and gives off hydrogen when treated with zinc, and gives no precipitation of sulphur when boiled with sulphuric acid. At a higher temp., A. Colefax, and A. F. Hollemann observed a reaction between the sulphur dioxide and thiosulphuric acid or sodium thiosulphate, resulting in the formation of a trithionate. A. F. Hollemann said that the secondary formation of trithionate by the action of sulphurous acid on undecomposed thiosulphate, does not take place to any appreciable extent because the acidity of the product decreases so slowly.

H. H. Landolt said that *die Existenzdauer*—the period of stability—of the acid, before the clear liquid becomes opalescent, (i) is independent of the nature of the acid employed to decompose the thiosulphate; (ii) is not influenced by an excess of either acid or thiosulphate; (iii) is independent of the vol. of the soln.; (iv) is proportional to the conc. of the thiosulphuric acid—temp. constant; and (v) is dependent on the temp. so that the higher the temp., the more rapid the decomposition. The acceleration of the velocity of decomposition per 10° rise of temp. is smaller the higher the temp., and is greater the more dil. the soln. The period of stability, t, for n parts by wt. of water per unit wt. of thiosulphuric acid when n ranges from 51 to 279, at a temp. $\theta°$ between 10° and 50°, was represented by $t=n(0{\cdot}6428-0{\cdot}02553\theta+0{\cdot}000272\theta^2)$. A. A. Winkelmann found the period of stability to be inversely proportional to the mean velocity of the liquid molecules. G. Gaillard showed that the presence of salts—chlorides, bromides, iodides, and sulphates –retards the appearance of the opalescence. On adding equal vols. of water, glycerol, and alcohol to the same vol. of acid, the greatest retardation occurs with alcohol, the least, by water. J. Aloy also found that the presence of neutral salts and of alcohol lengthened the period of stability; and H. H. Landolt, and H. Rössler also found that the thiosulphuric acid appears to be more stable in alcoholic soln.; and the latter said that an alcoholic soln. was not all decomposed after standing five months. H. H. Landolt said that light and electric sparks have no influence on the decomposition, but J. Aloy found that sunlight accelerates the decomposition.

H. von Oettingen interpreted his observations on the decomposition of thiosulphuric acid in terms of the ionic theory, and represented the reaction by: $S_2O_3''+H^{\cdot}=HSO_3'+S$, so that the conc., C, of the $H^{\cdot}$-ions determines the progress of the reaction. If t denotes the time which elapses between the acidification of the dil. soln. of sodium thiosulphate and the appearance of the turbidity, for hydrochloric acid, $t=\{0{\cdot}01111 \log (1+0{\cdot}80C)\}^{1}$. With isohydric soln. of hydrochloric, oxalic, dichloracetic, or trichloracetic acid, the value of t remains unchanged. This is said to support the ionic theory. Sodium sulphite hinders the appearance of the turbidity, but the same values of t are obtained provided an allowance be made for the appropriation of the $H^{\cdot}$-ions by the SO_3''-ions to form either HSO_3'-ions or non-ionized mols. of sulphurous acid. The equilibrium condition for the reaction: $R_2S_2O_3 \rightleftharpoons R_2SO_3+S$ could not be determined because of the consecutive reaction between the thiosulphate and the sulphite. C. K. Jablczynsky and Z. Watszawska-Rytel measured the degree of opacity with time and found the resulting curve is characteristic of a typical autocatalytic reaction. Hydrogen ions accelerate the reaction considerably, but sodium ions have little effect, so that mechanical coagulation appears to play little part in the process. Dilution of the soln. or addition of sulphurous acid or protective colloids retards the reaction. It is suggested that the reaction consists of the decomposition of the thiosulphuric acid according to the unimolecular law, followed by the aggregation of the sulphur formed into nuclei which catalyze the decomposition of the acid and render the soln. turbid. K. Jablczynsky and co-workers, and E. Paxeddu, R. P. Sanyal and N. R. Dhar studied the period of induction. G. I. Pokrowsky found that the variation of the diameter of the particles, η, as a function of the time, t, and the conc., C, of the thiosulphate soln. is given empirically by $\eta=\eta_0(1-e^{-aCt})$, where a and η_0 are constants. According to A. F. Hollemann, the decomposition of thiosulphuric acid is unimolecular: $H_2S_2O_3=H_2O+SO_2+S$; and the reaction should therefore be fastest at the outset when the conc. is a maximum. The period of induction is only make-belief; the formation of sulphur takes place from the commencement, but takes time to form visible aggregates. This is indicated by neutralizing the mixture of acid and thiosulphate before the turbidity appears, when the sulphur becomes visible after the usual interval. This would mean that peptizing agents for sulphur should delay the appearance of the opalescence. W. Biltz and W. Gahl examined thiosulphuric acid under the ultra-microscope and inferred that the process is not continuous, for a discontinuity becomes apparent at about the same moment as the opalescence is visible to the naked eye. Colourless supersaturated soln. of the acid in water can therefore exist. Colloidal aq. soln. of the acid are blue, and very unstable. R. Engel, A. Colson, J. Fritzsche, and M. Berthelot discussed the character of the sulphur which separates when thiosulphates are treated with acids—*vide* the allotropic forms of sulphur. W. Ostwald assumed that the instability of thiosulphuric acid is due to the reducing action of $H^{\cdot}$-ions on S_2O_3''-ions; A. F. Hollemann said that undissociated mols., not ions, take part in the reaction, because the equilibrium between the undecomposed mols. and free ions which must be maintained—the recombination of the ions would lead to a retardation and ultimate stoppage of the action at the concentration where the ions no longer re-unite, so that the constant k in the equation $-dC/dt=kC$ will vary in the same sense as the concentration C; if the reaction occurs between ions, the constant and concentration would vary in opposite senses, and this is not in accord with the observed results. For $0{\cdot}5N$-, $0{\cdot}2N$-, and $0{\cdot}1N$-soln., k was found to be respectively 0·437, 0·258, and 0·068. H. Bassett and R. G. Durrant found that the reaction follows a bimolecular course. Although the reaction is really a complex one involving three concurrent processes, $H_2S_2O_3\rightleftharpoons H_2SO_3+S$; $2H_2S_2O_3=H_2S+H_2S_3O_6$; and $2H_2S_2O_3\rightleftharpoons H_2O+H_2S_4O_5$, yet the conditions can be so arranged that 50 to 70 per cent. of the decomposition involves the reaction $H_2S_2O_3\rightleftharpoons S+H_2SO_3$, and, since the process is bimolecular, the equation $2H_2S_2O_3\rightleftharpoons 2H_2SO_3+S_2$ probably describes the process better than the one previously given. F. C. Gil and J. Beato concluded that the soln. of thiosulphuric acid becomes more stable the greater the acidity of the soln., hence, it becomes less stable the greater the alkalinity of the soln. This is not true; with soln. of low acidity thiosulphate decomposes more quickly than with soln. of greater acidity. H. Bassett and R. G. Durrant observed that with soln. of increasing acidity, the time taken for the appearance of the sulphur passes through a minimum, Fig. 107, and with high acidity, no sulphur separates until after many hours. This delay is not due, as F. Förster and R. Vogel suppose, to the retarding influence of conc. hydrochloric acid on the reaction: $HS_2O_3'=HSO_3'+S$, but both the reactions $H_2S_2O_3\rightleftharpoons H_2SO_3+S$, and $2H_2S_2O_3\rightleftharpoons H_2S+H_2S_3O_6$ are accelerated by acid, the former more than the latter because the greater part of the sulphurous acid becomes sulphur dioxide and water. These consecutive reactions are favoured by acids as well as $H_2S+H_2S_2O_5\rightleftharpoons HO.S.O.S.OH+(HO)_2S$, and $(HO)_2S+H_2S\rightleftharpoons 2S+2H_2O$; the reactions $H_2S_3O_6+S=H_2S_4O_6$, and $H_2S_4O_6+S=H_2S_5O_6$ are also favoured by acids. Hence, although increasing acidity favours the rapid separation of sulphur, yet it lengthens the time required for the appearance of the sulphur by favouring all the opposing reactions. Hence a minimum time for the appearance of sulphur at a fairly definite acidity could be anticipated. The non-appearance of sulphur does not mean that no decomposition has occurred. The decomposition probably begins as soon as the thiosulphuric acid is liberated from its salts. The non-appearance of sulphur is not, as A. F. Hollemann suggested, due to the separated sulphur remaining in the colloidal condition, but because the sulphur is consumed faster than it is separated owing to the formation of polythionic acids. H. Bassett and R. G. Durrant added that all the reactions occurring in the acidified thiosulphate proceed with a diminution of acidity. They gradually become slower as the limiting

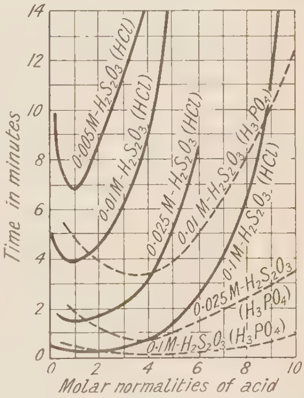


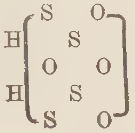
FIG. 107.—Times of the Appearance of Sulphur in Acidified Solution of Thiosulphate.

conc. of the several polythionic acids characteristic of the prevailing hydrogen-ion conc. are approached. Since the hydrogen-ion conc. gradually diminishes, the system is never fully stable—readjustments are continually necessary which ultimately lead to the decomposition of the polythionic acids with separation of sulphur. T. Salzer, and F. Raschig studied the marked influence of arsenic trioxide in preventing the separation of sulphur, and promoting the formation of pentathionic acid from thiosulphate. Sulphur oxidizes arsenite to oxysulpharsenate. H. Bassett and R. G. Durrant said that the oxysulpharsenate acts in two ways: (i) owing to its ready formation, it prevents the separation of sulphur by the reaction $H_2S_2O_3 \rightleftharpoons H_2SO_3 + S$ owing to the direct reaction: $H_2S_2O_3 + H_3AsO_3 \rightleftharpoons H_2SO_3 + H_3AsO_3S$—assuming that this is the only oxysulpharsenate involved in the reaction. The oxysulpharsenate yields its sulphur to the trithionate formed in the reaction $2H_2S_2O_3 \rightleftharpoons H_2S + H_2S_3O_6$ to give tetrathionic and pentathionic acids. (ii) It can take up any sulphur formed in the secondary reactions: $H_3AsO_3 + S \rightleftharpoons H_3AsO_3S$. Under favourable conditions, complete conversion of thiosulphate into pentathionate is theoretically possible with the help of small quantities of arsenious oxide, and very good yields are actually obtainable. It will be observed that the arsenious acid is really a vehicle for the handing on of sulphur to trithionic acid just as is sulphurous acid, the oxythioarsenic acid playing the same rôle in the one case as thiosulphuric acid in the other.

Returning to Fig. 106, H. Bassett and R. G. Durrant added that if dil. soln. of thiosulphate be treated with less acid than corresponds with the minima in the curves, and then quickly neutralized before sulphur becomes visible, separation of sulphur may be entirely prevented if the addition of alkali has been made an appreciable time before precipitation would normally occur. If, however, the alkali is added very shortly before separation of sulphur would occur normally, its addition causes immediate separation of sulphur, and in such cases either alkali or lanthanum nitrate will produce a precipitate. Soln. to the right of the minima still give the reactions for colloidal sulphur with separation of sulphur on addition of alkali or lanthanum nitrate, but it is probable that they also contain pentathionate (although this is difficult to prove), the proportion of pentathionate increasing with acidity and time and that of colloidal sulphur diminishing.

In strongly acidified soln. of thiosulphuric acid, the reaction $H_2S_2O_3 \rightleftharpoons H_2SO_3 + S$ is delayed, so also is the formation of pentathionic acid. This makes it appear as if the thiosulphuric acid becomes more stable. H. Bassett and R. G. Durrant explain the facts by assuming that the thiosulphuric acid also decomposes in accord with the reversible reaction $2H_2S_2O_3 \rightleftharpoons H_2O + H_2S_4O_5$. The acid $H_2S_4O_5$ is thus formed by the condensation of two mols of thiosulphuric acid with the elimination of water. In dil. soln., the active mass of the water would prevent the reaction proceeding very far. A conc. soln. of zinc chloride greatly delays the separation of the sulphur owing presumably to its dehydrating action. It is assumed that the anhydro-acid, *dithiodisulphuric acid*, or *dithiopyrosulphuric acid*, $H_2S_4O_5$, is more stable towards a loss of sulphur or hydrogen sulphide than is thiosulphuric acid; but in other directions it behaves very like thiosulphuric acid. Thiosulphate soln. which have been treated with a large excess of conc. hydrochloric acid still reduce iodine; they also exert a strong bleaching action on indigo, methylene-blue, litmus, and methyl-orange. The amount of methylene-blue which is bleached is in close agreement with the equation: $C_{10}H_{18}N_3SCl + H_2S_4O_5 + H_2O \rightleftharpoons C_{10}H_{19}N_3S.HCl + H_2S_4O_6$. The rate at which the methylene-blue is bleached is very greatly increased by rise of temp. The strongly acidic bleached solutions are comparatively stable towards atmospheric oxidation, but the blue colour is at once restored by a drop or two of strong nitric acid, by hydrogen peroxide, or even by silver nitrate or silver acetate. There is no evidence of the formation of a colourless addition compound between a mol of methylene-blue and a mol of dithiodisulphuric acid or two mols of thiosulphuric acid. The dithiodisulphuric acid which acts on methylene blue is supposed to originate from the two reactions

$2H^{\cdot}+2S_2O_3'' \rightleftharpoons 2HS_2O_3'$, and $2HS_2O_3' \rightleftharpoons S_4O_5''+H_2O$, which are equivalent to $2H+2S_2O_3'' \rightleftharpoons S_4O_5''+H_2O$. The rates of bleaching of methylene-blue with varying conc. of sodium thiosulphate and of hydrochloric acid are in agreement with this. The dithiodisulphuric acid is supposed to be formed by the elimination of a mol of water from two hydroxyl-groups, and not from one hydroxyl-group and one thionyl-group, and to have the structure:



If, and when, either of the hydrogen-ions ceases to be ionized, it can become attached by covalencies to either a sulphur or an oxygen atom. Three tautomeric structures are thus possible for the non-ionized $H_2S_4O_6$ just as two are possible for non-ionized thiosulphuric acid.

The preparation of the thiosulphates has been discussed in connection with sodium thiosulphate—*vide infra.* They are obtained:

1. By the action of sulphur—(i) On the alkali or alkaline earth hydroxides or carbonates. (ii) On the alkali or alkaline earth sulphates, chromates, or phosphates.
2. By the action of hydrogen sulphide or the sulphides—(i) On sulphur dioxide or the sulphites. (ii) On manganese dioxide. (iii) On various alkali salts. (iv) On tetrathionates. (v) On electrolysis.
3. By the action of polysulphides—(i) When oxidized by air. (ii) When the aq. soln. is boiled. (iii) When oxidized by dichromates, etc.
4. By the action of sulphur dioxide or sulphites—(i) On sulphur. (ii) On hydrogen sulphide or sulphides. (iii) On metals or metalloids. (iv) On boiling with formic acid. (v) On electrolysis.
5. Miscellaneous processes—in the decomposition of hyposulphites; tri-, tetra-, and pentathionates; and nitrogen sulphide.
6. Biological processes.

C. A. Valson[4] represented the capillary modulus of the radicle S_2O_3 by 1·4. J. Thomsen calculated the heat of formation of thiosulphuric acid to be $(SO_2,S,Aq.)=-1{\cdot}57$ Cals.; $(SO_2aq.,S)=-9{\cdot}27$ Cals.; $(2S,3O,H_2,Aq.)=137{\cdot}86$ Cals.; $(2S,O_2,Aq.)=69{\cdot}5$ Cals.; and M. Berthelot gave for octahedral sulphur $(2S,O_2,H_2O,Aq.)=79{\cdot}4$ Cals. For the heat of oxidation to sulphuric acid, J. Thomsen gave 215·346 Cals.; and for the heat of neutralization, 28·97 Cals. J. A. Muller measured the amount of heat absorbed when a mol of thiosulphuric acid is treated with one mol and with two mols of hydrochloric acid. The heat due to the formation of $NaHS_2O_3$ in the one case is nearly equal to that due to the formation of $Na_2S_2O_3$ from $H_2S_2O_3$, when the reactions occur at such dilutions that the changes due to secondary reactions are negligible. Hence, the "acid energies" of the two hydrogen atoms of thiosulphuric acid are nearly the same. A. Lindh observed that the X-ray absorption spectrum of the thiosulphates shows limits of absorption corresponding with bivalent and sexivalent sulphur.

A. F. Hollemann gave the mol. conductivity, μ, to be of the same order as that of sulphuric acid, and much above that of acetic acid. $\mu=274{\cdot}6$ for a mol of the acid in 32 litres of water; and for the ionic velocity for the $\frac{1}{2}S_2O_3''$-ion 78·8 calculated from sodium thiosulphate; and G. Bredig calculated 91 from magnesium thiosulphate. According to K. Jellinek, the first ionization constant of thiosulphuric acid $[H^{\cdot}][HS_2O_3']=K_1[H_2S_2O_3]$ is probably as great as that of sulphuric acid, $K_1=0{\cdot}45$; while from A. F. Hollemann's measurements for sodium thiosulphate, the value of K_2 in $[H^{\cdot}][S_2O_3']=K_1[HS_2O_3']$ is 0·0104, which is nearly the same as that of sulphuric acid. K. Jellinek, therefore, concluded that the strength of the acid function of oxygen and sulphur is about the same. I. M. Kolthoff held that sulphur has a stronger electronegative action than oxygen, and he found for K_2 of thiosulphuric acid, K_2 0·057 at 15°. F. R. Bichowsky gave $-125{,}110$ cals.

for free energy of formation of the thiosulphate ion at 25°. F. J. Factor said that the ions with soln. of sodium thiosulphate are $Na^{\cdot}$, and S_2O_3'', but at a higher temp. $Na^{\cdot}$- and NaS_2O_3'-ions are formed. He found that when a soln. of sodium thiosulphate is electrolyzed there are formed sulphur, hydrogen sulphide, tetrathionic acid, sulphur dioxide, and sulphuric acid. C. J. Thatcher found that when sodium thiosulphate is electrolyzed using a platinized cathode, tetrathionate is produced so long as the soln. remains neutral or faintly alkaline; whereas if the soln. becomes acidic or strongly alkaline, other reactions occur producing sulphur, sulphite, and sulphate. The formation of sulphate in a strongly alkaline soln. is attributed to the presence of trithionate which is produced along with thiosulphate by the hydrolysis of the tetrathionate. The trithionate is then oxidized to sulphate; the tetrathionate is not oxidized in neutral or acidic soln. The electro-oxidation of thiosulphate to tetrathionate occurs with an anode potential difference of —0·75 to —0·95 volt; and the oxidation is not regarded as a direct secondary chemical process of oxidation by, presumably, oxygen formed in the primary process of electrolysis. This chemical oxidation is accelerated by the platinized electrode, for if the platinum is clean and bright, the amount of oxidation for the same amount of electricity is much smaller. That the oxidation of thiosulphate is an indirect process is deduced from the variation of the potential-current curves with the conc. of the various ions involved; by this means, it is shown that hydroxyl or oxygen ions are discharged at the electrode. Further, the influence of certain non-dissociated "poisons"—such as mercuric cyanide—on the potential difference between platinum and thiosulphate soln. shows that in the process $S_2O_3'' \rightarrow S_4O_6''$ oxygen or some compound of oxygen is involved, and that the metal of the electrode acts catalytically. The mechanism of the reaction is, therefore, represented $O^{\cdot\cdot}+\ominus=\frac{1}{2}O_2$; and $2S_2O_3''+\frac{1}{2}O_2=S_4O_6''+O''$—*vide infra*, ammonium and sodium thiosulphate. J. Scheffer and F. Böhm observed that the reduction potential of thiosulphate→tetrathionate in an atm. of nitrogen is not constant for $E_H=0·323$ volt at the beginning, and 0·218 volt after 26 hrs. The reaction $2S_2O_3''+2\oplus \rightleftharpoons S_4O_6''$ is reversible, and the normal potential of $S_2O_3 \rightarrow S_4O_6$ in neutral soln. is nearly 0·40 volt.

The chemical properties of the thiosulphates.—The thiosulphates with water of crystallization lose their water at 100°–215°. This subject was studied by O. Döpping,[5] C. Pape, and E. A. Letts—*vide* the individual salts. At higher temp., in the absence of air, sulphates and polysulphides are formed as shown by H. Rose, L. N. Vauquelin, M. Berthelot, and C. F. Rammelsberg with the alkali and alkaline earth thiosulphates (*q.v.*). A. Jacques observed that with a rapid rise of temp., sodium thiosulphate forms the sulphite, and sulphate as well as hydrogen sulphide and sulphur. When the thiosulphate is heated in **hydrogen,** it is reduced to a sulphide. When sodium thiosulphate is heated in **air,** F. Chaussier said that the sulphur burns. According to J. L. Gay Lussac, aq. soln. of the thiosulphates remain unchanged when exposed to air, but if over 2 mols of potassium hydroxide are present per mol of thiosulphate, oxidation occurs: $K_2S_2O_3+2KOH+2O_2=2K_2SO_4+H_2O$. S. U. Pickering found that the sodium salt is more stable than the potassium salt; the soln. is more stable if light be excluded, and, in agreement with A. V. Harcourt, in the liquid made alkaline with potassium hydroxide, but ammonium carbonate acts unfavourably. W. Petzold found that in the presence of acids, thiosulphates are first polymerized to pentathionates, $5S_2O_3''+10H^{\cdot}=2S_5O_6''+4H^{\cdot}+3H_2O$; but thiosulphate may be regarded as an end-product in the decomposition of aq. soln. of the polythionates—*i.e.* the tri-, tetra-, and penta-thionates. E. Collard found that a $0·1N$-$Na_2S_2O_3$ remained unchanged in concentration for 3½ years; but J. Davidsohn found that the soln. slowly decreased in strength, and not always, as E. Abel supposed, owing to the presence of traces of copper. I. M. Kolthoff also found that soln. of sodium thiosulphate decompose more rapidly in light than in darkness. The oxidizing action of air may be prevented to some extent by covering the soln. with a layer of light petroleum. The presence of alkaline substances prevents the decomposition almost completely. The addition of about 0·2 grm. of sodium carbonate per litre is sufficient to ensure in great measure the stability of the soln. The accelerative effect of deposited sulphur on the decomposition is probably due to bacterial action. The decomposition may be retarded by the addition of 0·01 grm. of mercuric iodide per litre of soln. F. L. Hahn and H. Windisch said that the addition of a very small amount of alkali enables thiosulphate soln. to be preserved without alteration in strength from the first day. The change which they otherwise suffer appears to be caused by the faintly acid reaction of distilled water; it certainly does not depend on the formation of sulphite or sulphide. According to A. Skrabal, 0·1N-soln. of sodium thiosulphate having an $H^{\cdot}$-ion conc. between $p_H=5$ and 12, after 5 months, had decreased 1·28 per cent. in strength, whilst soln. with $p_H=9$ to 10 had not changed. Soln. of greater acidity than this did not obtain a constant titre at any time during the tests, and, in the case of soln. of $p_H=5$ to 6 sulphur separated during the first few weeks and then gradually redissolved. Both hydrogen sulphide and sulphur dioxide could be detected at different times in these soln., so that they probably contained polythionic acids after prolonged storage. The addition of small quantities of copper sulphate lowered the titre even of the more alkaline soln. E. Abel showed that traces of copper favour the ageing of soln. of sodium thiosulphate, by reactions symbolized: $2Cu^{\cdot\cdot}+2S_2O_3''=2Cu^{\cdot}+S_4O_4''$; $2Cu^{\cdot}+\frac{1}{2}O_2\rightarrow 2Cu^{\cdot\cdot}+O''$; $O''+2H^{\cdot}\rightarrow H_2O$. The function of the carbon dioxide is to form carbonic acid and thus provide the necessary hydrogen- ions, since otherwise the catalyst would be precipitated and rendered practically inactive by the hydroxyl-ions. Stabilization of the soln. by addition of alkali (or corresponding compounds which neutralize acids and precipitate copper) is thus satisfactorily explained. The automatic stabilisation of the soln. by ageing is due, not only to consumption of the dissolved carbon dioxide, but also to loss of catalytic activity of the copper. F. Feigl suggested that the alteration of thiosulphate soln. on keeping may be due to the decomposition of the thiosulphate into sulphate and sulphur which, under the influence of hydrogen-ions or of carbon dioxide, combine to form the co-ordination complex [SO **S** OO]Na_2. K. Jablczynsky and co-workers studied this reaction—*vide supra*, the action of light. M. and M. L. Kilpatrick found that freshly-boiled, redistilled water yields a soln. of thiosulphate that is more stable than a soln. made with ordinary laboratory distilled water, ordinary distilled water, or redistilled water through which carbon dioxide-free air has been bubbled. Carbon dioxide, oxygen, and dilute sodium hydroxide have very little effect on the stability of soln. of sodium thiosulphate. The decomposition in these soln. may be caused by bacteria. N. N. Mittra and N. R. Dhar found that in the simultaneous oxidation of sodium sulphite (primary reaction) and thiosulphate (secondary reaction), the speed of the primary reaction is reduced. According to W. Gluud, at 100°, in contact with air under 10 atm. press., sodium thiosulphate undergoes total transformation into sulphate, provided that sufficient alkali is present to unite with the sulphuric acid formed from the sulphur; if such excess of alkali is lacking, part of the sulphur separates in a free state. A lower press. than 10 atm. may be used, but in such case either the temp. must be raised or the duration of the action increased. C. Mayr found that the prolonged passage of a current of pure air or of pure carbon dioxide or of a mixture of both through thiosulphate solutions prepared from freshly-boiled water causes no change in the titre, but exposure of the same soln. to ordinary air soon results in the deposition of sulphur, and first a slight increase, then a more rapid decrease in the titre. This has been proved to be due to inoculation of the soln. with sulphur bacteria derived from the air; in the presence of carbon dioxide, the bacteria thrive to a limited extent and cause first the decomposition of the thiosulphate into sulphur and sulphite, and then the oxidation of the sulphite to sulphate. The immersion of a piece of bright copper wire in a sterilized thiosulphate soln. results in a similar decomposition which is more rapid the higher the temp. A. Nathansohn,

G. J. Fowler and co-workers, W. T. Lockett, and W. Lasch studied the oxidation of thiosulphates by bacteria. C. Mayr and E. Kerschbaum studied the decomposition of soln. of sodium thiosulphate and said that there are three active kinds of bacteria. One causes the reaction: $2Na_2S_2O_3+H_2O+O=Na_2S_4O_6+2NaOH$; a second: $Na_2S_2O_3=Na_2SO_3+S$ and $Na_2SO_3+O=Na_2SO_4$; and a third, $2Na_2S_2O_3+H_2O+O=Na_2S_4O_6+2NaOH$ and $S+3O+H_2O=H_2SO_4$. One vol. per cent. of amyl alcohol sterilizes the soln. C. F. Capaun found that when **water** and sodium thiosulphate are heated in a sealed tube, sulphur and sodium sulphite are formed; if air be present, sulphate is produced. The hydrolysis of benzyl thiosulphate by alkali-lye was found by T. S. Price and D. F. Twiss to furnish sodium sulphite, benzyl disulphide, and thiobenzoic acid, and E. Fromm and F. Erfurt, also benzylsulphuric acid. E. Pietsch and co-workers studied the surface conditions in the efflorescence of the salt.

E. H. Riesenfeld and T. F. Egidius found that neutral soln. of thiosulphate react with ozone, forming sulphate and dithionate, but alkaline soln. give off oxygen so that two atoms of the ozone are active. According to A. Nabl, the reaction of aq. soln. of sodium thiosulphate with **hydrogen dioxide** can be represented: $2Na_2S_2O_3+H_2O_2=Na_2S_4O_6+2NaOH$, provided the alkali hydroxide be neutralized as fast as it is formed, otherwise, the tetrathionate is decomposed: $2Na_2S_2O_3+7H_2O_2=2Na_2SO_4+H_2S_2O_6+6H_2O$, and the dithionic acid is converted to sulphuric acid: $H_2S_2O_6+H_2O_2=2H_2SO_4$. He also suggested that in neutral soln., a compound, possibly $HO.S_2H$, is formed. R. Willstätter observed that if the sodium thiosulphate and hydrogen dioxide are in the molar proportion 1 : 2, a mixture of sulphate and trithionate is formed: $3Na_2S_2O_3+4H_2O_2=2Na_2S_3O_6+2NaOH+3H_2O$; and $Na_2S_2O_3+2NaOH+4H_2O_2=2Na_2SO_4+5H_2O$; unlike A. Nabl, he observed no formation of tetrathionate, as in the case of sodium sulphite. A. Casolari represented the reaction: $Na_2S_2O_3+4H_2O_2+H_2O=Na_2SO_4+H_2SO_4+4H_2O$. If the hydrogen dioxide be quite neutral, no alkalinity with phenolphthalein appears in the interaction with a thiosulphate; but with methyl-orange, an alkalinity corresponding with $2Na_2S_2O_3+H_2O_2=Na_2S_4O_6+2NaOH$ appears. As time goes on, the alkalinity of the liquid towards methyl-orange gradually diminishes, and the whole of the thiosulphate finally exists as sulphate. When the reaction takes place in presence of a salt the corresponding hydroxide of which is insoluble, such as a zinc, nickel, or cobalt salt, there is immediate precipitation of the hydroxide, and the soln. remains perfectly neutral; in this manner any possible action of the hydroxyl ions on the ions derived from the dissociation of the thiosulphate is avoided. The calculation of the alkalinity developed from the amount of metallic hydroxide precipitated shows that this alkalinity is exactly double that indicated by methyl-orange, so that the whole of the sodium thiosulphate is transformed into sodium hydroxide, according to the equation: $Na_2S_2O_3+H_2O_2=2NaOH+S_2O_3$. There is then a further action, represented in the cold probably by $4S_2O_3+5H_2O_2=H_2S_4O_6+4H_2SO_4$, which is in accord with A. Nabl's results; and in hot soln. by $4S_2O_3+5H_2O_2=H_2S_3O_6+4H_2SO_4+S$, which agrees with R. Willstätter's results. Hence, under these conditions, hydrogen dioxide can cause the complete dissociation of sodium thiosulphate into $2Na^{\cdot}$ and S_2O_3'', the formation of tetrathionate being due to a secondary action of the S_2O_3 anion with excess of the dioxide, whilst trithionate is formed as the result of decomposition of the tetrathionate by heat. F. Ferràboschi observed that no ozone is formed when sodium thiosulphate is oxidized with hydrogen dioxide. If a denotes the conc. of hydrogen dioxide, and b that of the sodium thiosulphate, E. Abel found that the reaction: $H_2O_2+2S_2O_3''+2H^{\cdot}=S_4O_6''+2H_2O$ in acidic soln. is bimolecular and can be represented by $dx/dt=k(a-x)(b-x)$, where the velocity constant $k=1{\cdot}53$. The reaction is accelerated by $H^{\cdot}$-ions. It is assumed that during the reaction there is an intermediate separation of electrically neutral S_2O_3-ions which determines the velocity of the reaction. Iodide-ions act catalytically on this intermediate reaction. The catalysis by iodide ions occurs in acetic acid soln.

provided enough acetate is present to reduce the conc. of the H$^{\cdot}$-ions. It is concluded (i) that the thiosulphate is oxidized with great velocity by hypoiodite directly to tetrathionate, according to the equation: $IO'+2S_2O_3''+2H^{\cdot}=S_4O_6''+I'+H_2O$; (ii) that the catalysis of the hydrogen dioxide and thiosulphate reaction by iodine ions does not necessarily require the intermediate separation of iodine, cases possibly occurring in which the reactions lead directly to the formation of the tetrathionate, that of the intermediate product, iodine, being completely suppressed, and (iii) that the decomposition of hydrogen dioxide by the catalytic action of iodine ions is a catalysis of an intermediate reaction, the first stage being directly detected by the reaction with thiosulphate. The addition of molybdic acid, even in the smallest concentrations, produces a far-reaching change in the nature of the reaction between hydrogen dioxide and thiosulphates.

The less energetic **oxidizing agents** convert thiosulphates into tetrathionates—*e.g.* hydrogen dioxide (A. Nabl),[6] iodine (M. J. Fordos and A. Gélis), potassium iodate (E. Sonstadt), cuprous chloride (F. Kessler), ferric chloride (M. J. Fordos and A. Gélis), and selenious acid (J. F. Norris and H. Fay). G. Jörgensen, and M. J. Fordos and A. Gélis observed that **chlorine** and **bromine** oxidize thiosulphates to sulphates: $Na_2S_2O_3+4Cl_2+5H_2O=Na_2SO_4+H_2SO_4+8HCl$; and they proposed it as an *antichlor* in the bleaching and papermaking industries as in the patent of M. Dambreville in 1846. G. Lunge said that the main reaction proceeds: $2Na_2S_2O_3+Cl_2=2NaCl+Na_2S_4O_6$, although some reacts in accord with M. J. Fordos and A. Gélis's equation: and possibly also: $Na_2S_2O_3+Cl_2+H_2O=Na_2SO_4+2HCl+S$. C. Mayr and J. Peyfuss represented the reaction with bromine in alkaline soln., $Na_2S_2O_3+4Br_2+5H_2O=Na_2SO_4+H_2SO_4+8HBr$; while iodine oxidizes the thiosulphates to dithionates. In alkaline soln., with chlorine or bromine it is probable that a **hypochlorite** or **hypobromite** is first formed, and, according to G. Lunge, when the thiosulphate is present in excess, the liquid becomes acid, and some hydrogen sulphide is evolved; presumably owing to the reaction: $2Na_2S_2O_3=Na_2S_3O_6+Na_2S$, followed by the decomposition of the sulphide by the acid. F. Raschig said that sodium hypochlorite oxidizes thiosulphate in acidic soln. giving partly sulphate and partly tetrathionate. A. W. Francis found the velocity constant of the oxidation of sodium thiosulphate with bromine to be 15. F. Diénert and F. Wandenbulcke found that in dil. soln. the reaction proceeds according to the equation $3Na_2S_2O_3+5Cl_2+5H_2O=Na_2SO_4+8HCl+H_2SO_4+Na_2S_4O_6+2NaCl$ or $5NaOCl+3Na_2S_2O_3+5H_2O=2Na_2SO_4+Na_2S_4O_6+5NaCl+5H_2O$. In the presence of acids, however, or even in the presence of sodium hydrocarbonate, much less sodium thiosulphate is required, the reaction being $Na_2S_2O_3+4Cl_2+5H_2O=2NaHSO_4+8HCl$. M. Berthelot said that in oxidizing the thiosulphate to sulphate, 150 Cals. of heat are liberated. For the action of **hydrochloric acid,** *vide infra*, formation of pentathionic acid: $Na_2S_2O_3+2HCl=SO_2+S+2NaCl+H_2O$. G. Vortmann gave $H_2S_2O_3=H_2S+SO_2+O$; and W. Vaubel: $H_2S_2O_3=H_2S+SO_3$. According to A. Kurtenacker and A. Czernotzky, the quantity of polythionate produced during the decomposition of *N*-sodium thiosulphate soln. by hydrogen chloride diminishes as the acid conc. is increased. Mercuric chloride, lead acetate, bismuth trichloride, sodium tungstate, or sodium sulphide soln. have no marked influence on the reaction. On acidifying a thiosulphate soln. which contains a small quantity of arsenite or arsenate, a strong odour of hydrogen sulphide is produced, which is rapidly replaced by that of sulphur dioxide; after some minutes a precipitate of sulphur and arsenious sulphide commences to form. For constant arsenic content, approximately equal quantities of tetra- and penta-thionate are formed at low acid conc.; at moderate conc. pentathionate alone is produced, whilst with higher conc. penta- and hexa-thionates are obtained. At constant acid conc. an increase of the quantity of arsenate in the soln. results in the formation of more tetrathionate, probably on account of partial neutralization of the acid present by the arsenite soln. Although an excess of arsenic acid should convert all the thiosulphate into tetrathionate, some pentathionate appears to be formed. Arsenious sulphide has no influence on the thiosulphate decomposition, and arsenic trichloride but little. Tervalent antimony has much less effect than has arsenious acid, whilst with molybdic acid the yield of polythionate is very small; in presence of stannic chloride considerable quantities of polythionate are produced. E. H. Riesenfeld and G. Sydow found that the decomposition of sodium thiosulphate in hydrochloric acid soln. alone thiosulphate may decompose according to either of the following schemes, depending on the acidity: (i) $S_2O_3''+H^{\cdot}=HSO_3'+S$, and (ii) $5S_2O_3''+6H^{\cdot}=2S_5O_6''+3H_2O$. The sulphurous acid formed in (i) then reacts with the pentathionic acid formed in the second reaction, giving first tetrathionic, then trithionic acid, thus (iii) $S_5O_6''+SO_3''=S_4O_6''+S_2O_3''$, and (iv) $S_4O_6''+SO_3''=S_3O_6''+S_2O_3''$. Trithionic acid may also be formed by the direct action of sulphurous acid on thiosulphuric acid, thus: (v) $S_2O_3''+4HSO_3'+2H^{\cdot}=2S_3O_6''+3H_2O$. In strongly acidic soln., however, trithionic acid decomposes rapidly as follows: (vi) $S_3O_6''=S+SO_2+SO_4''$. The addition of arsenious acid to the reaction mixture of hydrochloric acid and thiosulphate retards the reaction (i) and in the absence of sulphurous acid reactions (iii), (iv), and (v) cannot take place. Hence pentathionic acid formed according to (ii) is practically the sole product of the reaction in the presence of arsenious acid. O. von Deines found that some hydrogen persulphide is formed by the action of $3N$-HCl on thiosulphate: $2H_2S_2O_3=H_2S_2+H_2S_2O_6$. It is assumed that sulphoxylic acid, H_2SO_2, or sulphoxylic anhydride, SO, acts as an intermediate product so that sulphur dioxide is reduced by sulphoxylic acid like it is by hypophosphorous acid, forming, in both cases, hydrogen persulphide.

M. J. Fordos and A. Gélis found that when **iodine** reacts with sodium thiosulphate, sodium tetrathionate is formed: $2Na_2S_2O_3+I_2=2NaI+Na_2S_4O_6$, which H. Hertlein represented: $4Na^{\cdot}+2S_2O_3''+I_2=4Na^{\cdot}+2I'+S_4O_6''$. The reaction was studied by F. O. Rice and co-workers, E. Müller and H. Kogert, H. Clos, S. Popoff and J. L. Whitman, and W. C. Bray and H. E. Miller. A. von Kiss and I. Bossanyi studied the temp. coeff. of the reaction, and the effect of the presence of neutral salts. S. U. Pickering found that a little thiosulphate is at the same time oxidized to sulphate, $NaHSO_4$, and the proportion increases with rise of temp. so that at 20°, 2·1 per cent. of the iodine is consumed in forming the hydrosulphate. The result is not affected by the conc. of the soln., the conc. of the potassium iodide, or the conc. of the hydrochloric acid present. G. Topf, C. Friedheim, R. H. Ashley, J. P. Batey, and E. Abel also found the oxidation may proceed further than the tetrathionate; while I. M. Kolthoff said that in neutral or weakly acidic soln., the reaction between iodine and thiosulphate takes place in accord with $2Na_2S_2O_3+I_2=Na_2S_4O_6+2NaI$. In weakly alkaline soln., part of the thiosulphate is oxidized directly to sulphate without the intermediate formation of tetrathionate. The side reaction may be represented in two stages: $I_2+OH'=HOI+I'$, followed by $4HOI+S_2O_3''+6OH'=2SO_4''+4I'+5H_2O$. In sufficiently strongly alkaline soln., all the thiosulphate may in this way be oxidized to sulphate. In strongly acidic soln., the reaction is as in neutral soln., the decomposition of the thiosulphate by the acid being slow in comparison with the formation of tetrathionate. A. Gutmann observed that a soln. of sodium ethyl thiosulphate does not react with $0{\cdot}1N$-iodine, it does not dissolve silver halides, nor does it give a blue soln. with a cupric salt, or form potassium thiocyanate with potassium cyanide. W. B. Morehouse observed that the absorption of X-rays after the reaction: $3KI+I_2+2Na_2S_2O_3=3KI+2NaI+Na_2S_4O_6$, was about 0·24 less than before; and in 70 per cent. alcohol soln., the reaction $I_2+2Na_2S_2O_3=2NaI+Na_2S_4O_6$ was about 0·36 per cent. less. According to K. Jablczynsky and co-workers, the velocities of the reactions between iodine in chloroform and aq. sodium thiosulphate and between benzoic acid in carbon tetrachloride and aq. sodium hydroxide, as in the case of other heterogeneous reactions, are controlled by the rates of diffusion through surface layers at the boundary of the phases, and the general equation is deduced: $K=(v/0{\cdot}4343t)\times\log c_0/c$, in which v is the volume of chloroform or carbon tetrachloride, c_0 the initial conc. of iodine or benzoic acid, and c the conc. after t. The velocity constant depended on the rate of stirring of the aqueous layer (the lower layer not being stirred) and that the temp. coeff. was much lower than for chemical processes. C. L. Cottrell found that the absorption of X-rays by iodine in the reaction $I_2+2Na_2S_2O_3=2NaI+Na_2S_4O_6$ is on the long wave-length side of the K-limit about 0·3 per cent. greater, and on the short wave-length side about 0·5 per cent. greater than for combined iodine. According to E. J. Maumené, the action of iodine on barium thiosulphate may form not only tetrathionate, but also hyposulphurous acid, $H_2S_2O_4$, and an enneathionic acid, $H_2S_6O_9$; indeed, seven acids in addition to the tetrathionic acid should be possible according to the proportions of iodine and of thiosulphate employed.

A. W. Francis found that iodine distributes itself between sodium hydrosulphite and thiosulphate in the ratio 0·41 : 0·59; and bromine gave nearly the same results. L. L. de Koninck found that **cyanogen iodide** dissolved in hydriodic acid yields tetrathionate with thiosulphate; and if dissolved in neutral potassium iodide, tetrathionate and sulphate are formed. C. Meineke represented the reaction with sodium thiosulphate and cyanogen iodide in acidic soln. by the equation $2CyI+4Na_2S_2O_3+2HCl=2Na_2S_4O_6+2NaCl+2NaI+2HCy$; and in neutral soln., 3 mols of cyanogen iodide react with 5 mols of sodium thiosulphate, producing one mol of sodium sulphate—due, it is assumed, to a secondary reaction between the alkali cyanide and tetrathionate. A. E. Dixon and J. Taylor represented the reaction with **cyanogen bromide** as involving first the production of alkali cyanide: $NaO.SO_2.SNa+CyBr=NaO.SO_2.SNa : CyBr=NaCy+NaO.SO_2.SBr$, followed by $NaO.SO_2.SBr+NaS.SO_2.ONa=NaBr+Na_2S_4O_6$, and the alkali cyanide reacts with the tetrathionate producing hydrogen cyanide, etc., as represented by the equation: $4CyBr+8Na_2S_2O_3+H_2O=Na_2SO_4+Na_2SO_3+2NaSCy+2HCy+3Na_2S_4O_6+4NaBr$. A. Kurtenacker showed that there is no such difference between the effect of cyanogen bromide and iodide as is here implied. In neutral soln. the reaction may be represented by the equation: $3CNBr+5S_2O_3''+H_2O=3Br'+2HCN+CNS'+SO_4''+2S_4O_6''$. In acidic soln. the thiosulphate goes entirely into tetrathionate according to the equation $BrCN+2S_2O_3''+H^{\cdot}=Br'+HCN+S_4O_6''$. This is probably also the primary reaction in neutral soln., for during the reaction the soln. become temporarily alkaline through the formation of sodium cyanide. The latter, however, reacts with tetrathionate according to the equation $3NaCN+Na_2S_4O_6+H_2O=NaCNS+Na_2SO_4+2HCN+Na_2S_2O_3$. The thiosulphate thus regenerated reacts further with halogen cyanide, and the net reaction is: $3CyBr+5S_2O_3''+H_2O=3Br'+2HCy+CyS'+SO_4''+2S_4O_6''$. According to L. L. de Koninck, **hypoiodites** oxidize thiosulphates as in the case with hypochlorites and hypobromites: $Na_2S_2O_3+4NaIO+H_2O=2NaHSO_4+4NaI$. W. Spring, and M. J. Fordos and A. Gélis found that **chloric acid,** or an acidified soln. of **potassium chlorate** oxidizes thiosulphates to tetrathionates. W. Feit and K. Kubierschky said that an acid soln. of **potassium bromate,** or **bromic acid,** completely oxidizes thiosulphates in acidic soln. to sulphuric acid and water. A. Casolari represented the reaction: $HBrO_3+6H_2S_2O_3=HBr+3H_2S_4O_6+3H_2O$, and the reaction was studied by F. Fischer and W. F. Tschudin. E. Sonstadt said that an acid soln. of **potassium iodate,** or **iodic acid,** oxidizes thiosulphates to tetrathionates; E. Riegler represented the reaction: $6Na_2S_2O_3+6HIO_3=3Na_2S_4O_6+5NaIO_3+NaI+3H_2O$; and C. F. Walker added that the reaction is more complex than this, being influenced by time and concentration. When all the thiosulphate has been converted into tetrathionate and iodide, more iodic acid liberates iodine. G. S. Jamieson represented the reaction: $Na_2S_2O_3+2KIO_3+2HCl=Na_2SO_4+K_2SO_4+2ICl+H_2O$. W. R. Levinson studied the catalytic effect of sodium thiosulphate on the reduction of iodates by sulphur dioxide.

When heated with **sulphur,** the thiosulphates are reduced to sulphides. When **hydrogen sulphide** is passed into a soln. of sodium thiosulphate, sulphur is precipitated, slowly at ordinary temp., but more quickly on warming the soln. W. Petzold[7] represented the reaction with hydrogen sulphide: $2H^{\cdot}+S_2O_3''+2H_2S=3H_2O+4S$. According to H. Bassett and R. G. Durrant, the sulphur is produced by the decomposition of the thiosulphate: $H_2S_2O_3=H_2SO_3+S$, and to the reactions $H_2S+H_2S_2O_5=HO.S.O.S.OH+S(OH)_2$, and $S(OH)_2+H_2S=2H_2O+2S$. When heated, the soln. becomes yellow owing to the formation of polysulphide, and if the passage of gas be discontinued, the whole of the precipitated sulphur ultimately dissolves. If the soln. is boiled for a sufficient time, the yellow colour disappears, and the soln. is then, as a rule, alkaline to phenolphthalein. If hydrogen sulphide is again passed in, more sulphur will be precipitated, and will dissolve on heating. During the boiling, all the reactions of decomposition which occurred during the passage of hydrogen sulphide are reversed with regeneration of thiosulphate, but during this period there is a tendency for sodium sulphide and sulphite to produce some free alkali owing to hydrolysis. The action of **sulphur dioxide** on soln. of thiosulphates was studied by H. Hertlein, M. Berthelot, N. Villiers, H. Clos, F. Overdick, W. Spring, etc. According to H. Debus, when potassium thiosulphate is dissolved in an excess of a conc. soln. of sulphurous acid, the intense yellow soln. can be kept without the separation of sulphur or other apparent change. Hydrochloric acid precipitates sulphur from the liquid; alcohol gives a crystalline precipitate containing some globules of sulphur; and barium chloride gives a mixed precipitate of barium thiosulphate, sulphate, and sulphite. Hence, potassium thiosulphate is decomposed by sulphurous acid into potassium sulphite and thiosulphuric acid, which remains unchanged in a large excess of sulphurous acid. With a smaller proportion of sulphurous acid, the liquid turns yellow and smells of sulphur dioxide, but loses both colour and odour in the course of a few days, and sulphur is precipitated. Absolute alcohol added to the decomposed soln. of potassium thiosulphate precipitates potassium trithionate, and pentathionate is found in the filtrate. Not half the amount of sulphur required by the equation $2K_2S_2O_3+3SO_2=2K_2S_3O_6+S$ is precipitated. Some tetrathionate also is formed. It is therefore inferred that sulphurous acid decomposes a portion of potassium thiosulphate, forming the sulphite and thiosulphuric acid which, by condensation, is transformed into pentathionic acid and then to potassium pentathionate. Part of the thiosulphuric acid decomposes into sulphur and sulphurous acid. Potassium sulphite and pentathionate form thiosulphate and trithionate. Hence, potassium trithionate is the chief product, and the tetrathionate and pentathionate, and sulphur are minor products: $6K_2S_2O_3+9SO_2=K_2S_5O_6+K_2S_4O_6+4K_2S_3O_6$. Less pentathionate and tetrathionate, and more trithionate are produced than is indicated by this equation because of the precipitation of sulphur: $2K_2S_2O_3+3SO_2=2K_2S_3O_6+S$. H. Bassett and R. G. Durrant consider that the presence of sulphurous acid favours the decomposition: $2H_2S_2O_3\rightleftharpoons H_2S+H_2S_3O_6$, by partly preventing the reaction $H_2S_2O_3\rightleftharpoons H_2SO_3+S$, partly by forming the yellow, stable complex $H_2S_2O_3.SO_2$, and partly by removing hydrogen sulphide. The sulphur which is formed under these conditions usually regenerates thiosulphate without being deposited. H. Hertlein obtained a quantitative conversion of thiosulphate into trithionate by acting on a sat. soln. of potassium thiosulphate with conc. sulphurous acid at 30°. Under ideal conditions the reactions which occur can be summarized by $K_2S_2O_3+4SO_2+H_2O=K_2S_3O_6+H_2S_3O_6$. Action does not cease with the formation of trithionate, the continued action of sulphurous acid causes hydrolysis of trithionate, and ultimately sulphate and sulphur appear; tetra- and penta-thionate may be formed in the intermediate stages. W. Feld represented the reaction between thiosulphates and sulphur dioxide: $2(NH_4)_2S_2O_3+3SO_2=(NH_4)_2S_3O_6+(NH_4)_2S_4O_6$, and F. Raschig said that the intermediate stages involve the formation and decomposition of pentathionate: $5Na_2S_2O_3+3SO_2=2Na_2S_5O_6+3Na_2SO_3$; followed by $2Na_2S_5O_6+3Na_2SO_3=Na_2S_3O_6+Na_2S_4O_6+3Na_2S_2O_3$. F. Förster and R. Vogel found that when a soln. of a thiosulphate is treated with an acid, it is inferred that the balanced reactions which occur can be symbolized $S_2O_3''+H^{\cdot}\rightleftharpoons HS_2O_3'$; and $HS_2O_3'\rightleftharpoons HSO_3'+S$, or (i) $S_2O_3''+H^{\cdot}\rightleftharpoons HSO_3'+S$, because the hydrosulphite and the thiosulphate on acidification furnish sulphur and sulphurous acid; changes in the conc. of the substances taking part of the reaction alter the equilibrium in accord with this equation; and when thiosulphate soln. are decomposed by weak acids, the equilibrium constant, on applying the law of mass action is $K=[S_2O_3''][H^{\cdot}]/[HSO_3']$, or $K=0{\cdot}13$ at 11°. The yellow colour of the thiosulphate soln., after the addition of an excess of sulphurous acid, is attributed not to colloidal sulphur, but rather to complex anions in which sulphur dioxide is co-ordinately linked to the thiosulphate ions—as exemplified by the formation of the complexes $K_2S_3O_3.SO_2$, etc.—and there is the balanced reaction: (ii) $S_2O_3''+SO_2\rightleftharpoons[S_2O_3(SO_2)]''$, which also involves (iii) $H^{\cdot}+HSO_3'\rightleftharpoons H_2SO_3\rightleftharpoons SO_2+H_2O$. By sufficiently acidifying the thiosulphate solutions, equilibrium (ii) can set in, with consequent yellow coloration of the soln. Since by the appearance of (ii) the conc. of thiosulphate is diminished, the separation of sulphur in (i) may be hindered by sufficiently lowering the hydrogen-ion conc. or increasing hydrogen sulphurous acid conc., *i.e.* the ratio of the conc. of sulphurous acid to that of thiosulphate must be somewhat greater than (i). According to (ii), it must be greater the smaller is the thiosulphate concentration; such solutions are yellow and remain completely clear for some time. The systems (i) and (ii) may change so that tri- or penta-thionates are formed: (iv) $5S_2O_3''+6H^{\cdot}\rightarrow 2S_5O_6''+3H_2O$; or (v) $S_2O_3''+4HS_2O_3'+2H^{\cdot}\rightarrow 2S_5O_6''+3H_2O$. The pentathionate may also change (vi) $S_5O_6''+HSO_3'\rightarrow S_4O_6''+S_2O_3''+H^{\cdot}$, and $S_4O_6''+HSO_3''\rightarrow S_3O_6''+S_2O_3''+H^{\cdot}$. The trithionate also decomposes: $S_3O_6''+H_2O\rightarrow SO_4''+S_2O_3''+2H^{\cdot}$, and the thiosulphate so formed enters into system (i). The acidified soln. of thiosulphate also passes into sulphur, sulphate, and sulphurous acid. A. Kurtenacker and A. Czernotsky observed that the yellow soln. obtained by treating a thiosulphate soln. with sulphur dioxide becomes colourless on keeping and then yields a precipitate of sulphur when treated with formaldehyde and sodium hydroxide or acetate, although no polythionate can be detected in the soln. Neutralization of the colourless liquid with sodium hydroxide yields thiosulphate and sulphite, but no precipitate of sulphur. With ice-cold conc. hydrochloric acid and thiosulphate a similar colourless soln. is obtained without precipitation of sulphur; after 15 hrs. no thiosulphate can be detected. These reactions are ascribed to the formation of a complex of sulphur and sulphurous acid; thus $[S_2O_3,SO_2]''+H_2O\rightleftharpoons[S_2O_3,SO_3H_2]''$; $[S_2O_3,SO_3H_2]''\rightleftharpoons[S(SO_3H)_2]''$.

For the action of **sulphuric acid** on the thiosulphates, *vide supra*. For H. Marshall's observation on the action of **persulphates** resulting in the formation of tetrathionates, *vide supra*. W. Spring found that **sulphur monochloride** or **sulphur dichloride** converts potassium thiosulphate into the tetrathionate. According to J. F. Norris and H. Fay, a soln. of **selenium dioxide** in dil. hydrochloric acid reacts: $SeO_2+4Na_2S_2O_3+4HCl=2Na_2S_4O_6+Se+4NaCl+2H_2O$, and in the presence of more conc. hydrochloric acid: $SeO_2+4Na_2S_2O_3+4HCl=Na_2S_4SeO_6+Na_2S_4O_6+4NaCl+2H_2O$; **tellurium dioxide** gives a yellow soln. from which sodium hydroxide precipitates tellurium. The reaction with selenious acid is discussed in connection with the selenothionic acids. J. T. Norton observed that salts of selenium and tellurium are reduced and the elements precipitated when heated with a soln. of sodium thiosulphate at 140°–200°.

E. C. Franklin and C. A. Kraus[8] found that sodium thiosulphate is easily soluble in liquid **ammonia.** J. L. Gay Lussac showed that thiosulphates are oxidized by **nitric acid** and aqua regia to sulphuric acid. L. Santi represented the reaction of a thiosulphate with a boiling soln. of **ammonium chloride**: $Na_2S_2O_3+2NH_4Cl=2NaCl+H_2O+2NH_3+SO_2+S$. R. F. Weinland and A. Gutmann found that the thiosulphates are not reduced by **nitrites**; when a small quantity of a mixed soln. of sodium nitrite and thiosulphate is evaporated to dryness and gently heated, a violent explosion occurs. According to P. Falciola, if a very dil. soln. of sodium thiosulphate be treated with a dil. soln. of alkali nitrite, and the liquid is then acidified with either an inorganic or organic acid or a salt, such as alum, giving an acid soln., more or less marked effervescence occurs and the soln. assumes a yellow colour which, according to the amounts of the substances used, may at first be green or orange-brown. The reaction is equally sensitive in aq. alcoholic soln., and is shown distinctly by 0·0001*N*-sodium thiosulphate, which does not readily yield sulphur when treated with a mineral acid or give a coloration with ferric chloride. Only excessive proportions and concentrations of sulphurous acid prevent the reaction with traces of thiosulphate. The nitrous ion in presence of the nitric ion may be detected by means of the reaction. A. Berthoud and W. E. Berger discussed the induction by sodium thiosulphate of the reaction between iodine and potassium nitrite. J. M. Eder recommended a 0·2 per cent. soln. of **chloroamine** for removing the last traces of thiosulphate from photographic plates. R. F. Weinland and A. Gutmann found that **hyposulphites,** and **phosphites** do not reduce sodium thiosulphate.

According to J. Y. Buchanan, **phosphorus pentachloride** reacts with lead thiosulphate, dried at 100°—not the hydrated salt (C. Pape)—forming hydrogen chloride, lead chloride, sulphur dioxide, sulphuryl chloride, and what is probably thiophosphoryl chloride. K. Kraut said that phosphorus pentachloride converts sodium thiosulphate into sulphate ; while **phosphoryl chloride** does not attack the anhydrous salt. F. J. Faktor heated **arsenic trioxide** with five times its weight of anhydrous sodium thiosulphate and obtained red arsenic disulphide and the yellow trisulphide ; and similar products were obtained with **arsenic pentoxide.** J. T. Norton found that arsenic is not precipitated as sulphide when its salts are treated with a soln. of sodium thiosulphate at 140°–200°, unless an acid be present—*vide infra*, arsenic thiosulphate ; and for G. S. Forbes and co-workers' observations on the clock reaction, *vide* arsenic trioxide. T. Salzer found that when sodium thiosulphate is treated with **sodium orthoarsenite** and hydrochloric acid, it forms pentathionic acid ; on the other hand, L. W. McCay represented the reaction which occurs when a mixture of the two salts is triturated with sodium hydroxide : $Na_3AsO_3+Na_2S_2O_3=Na_3AsO_3S+Na_2SO_3$. R. F. Weinland and A. Gutmann added that the products of the reduction when soln. of the two salts are mixed are sodium sulphite and sodium sulphotrioxyarsenate, while a small quantity of arsenic is precipitated ; with the potassium salts the products are similar ; while with calcium thiosulphate and sodium arsenite, a precipitate of calcium arsenite is formed, and on heating the mixture, sodium and calcium sulphotrioxyarsenates are formed. A. Gutmann represented the reaction with sodium ethylthiosulphate and sodium arsenite in the presence of sodium hydroxide : $2Na(C_2H_5)S_2O_3+2NaOH+2Na_3AsO_3=2Na_2SO_3+2C_2H_5SH+2Na_3AsO_4$. According to R. F. Weinland and A. F. Gutmann, at ordinary temp. sodium thiosulphate and **sodium hydroarsenite** form sodium sulphotrioxyarsenate and sulphite, and a little arsenic ; when heated a yellowish-red product containing no sulphoxyarsenate is formed. The corresponding potassium salts behave similarly. Sodium thiosulphate reacts with **sodium dihydroarsenite**, forming sodium sulphite, arsenic is precipitated, and then red arsenic disulphide. The mother-liquor deposits a sulphoxyarsenate when heated on the water-bath. F. J. Faktor found that when a mixture of **antimony trioxide** with five times its weight of sodium thiosulphate is heated to redness, greyish-black antimony trisulphide is formed. J. T. Norton found that antimony is completely precipitated as sulphide when its salts are treated with soln. of sodium thiosulphate at 140°–200°. M. Meyer arranged the reaction between thiosulphates and antimony salts (*q.v.*) as a clock reaction—*vide infra*, antimony thiosulphate. R. F. Weinland and A. Gutmann observed that when sodium thiosulphate is heated with a conc. soln. of **sodium antimonite**, it is reduced to sulphite, and sodium pyroantimonate and sulphoantimonate are formed ; with potassium salts, potassium antimonate and sulphoantimonate are produced, and if the mixture is allowed to stand at ordinary temp., antimony trisulphide is precipitated, and the mother liquid contains potassium disulphodioxyantimonate.

When sodium thiosulphate and **carbon** are heated together, sodium sulphide is formed—*vide supra*, for the action of cyanogen halides. I. M. Kolthoff[9] studied the influence of charcoal on the velocity of decomposition of thiosulphuric acid. H. von Pechmann and P. Manck found that when heated with **potassium cyanide,** thiocyanate is formed. According to H. Rose, **mercuric cyanide** makes the soln. of sodium thiosulphate alkaline, but no precipitate is formed, and very little sulphide is produced, but when an acid is added, a white precipitate is formed. A. Gutmann observed that in neutral soln., mercuric cyanide and barium thiosulphate react according to the equation: $Hg(Cy)_2+2BaS_2O_3+H_2O=HgS+BaSO_3+BaSO_4+HCy+HCyS$, whilst the reaction in alkaline soln. is represented by $4Hg(Cy)_2+8Na_2S_2O_3+Na_2O=3Hg(CyS)_2+NaCyS+NaCy+HgS+7Na_2SO_3+Na_2SO_4$, from which it appears probable that thiosulphuric acid exists in two tautomeric forms. F. Kessler's reaction takes place in acid soln.: $Hg(Cy)_2+BaS_2O_3+H_2O=HgS+2HCy+BaSO_4$ and $BaS_2O_3+2HCl=BaCl_2+SO_2+S+H_2O$. Mixtures of soln. of mercuric cyanide and sodium ethyl thiosulphate soon become acidic,, owing to the reaction: $2NaSO_2.OSC_2H_5+HgCy_2+2H_2O=2NaHSO_4+2HCy+Hg(SC_2H_5)_2$. For H. Bunte's observations on the action of **ethyl bromide,** *vide infra*, the constitution of thiosulphates. A. Kappanna studied the kinetics of the reaction of the thiosulphates on **sodium bromoacetate.** F. C. Calvert said that a soln. of sodium thiosulphate 1 : 1000 does not affect protoplasmic life nor fungi. When sodium thiosulphate is mixed with a yeast-sugar fermentation mixture, C. Neuberg and E. Welde found that 15 per cent. is reduced in accord with $Na_2S_2O_3+H_2=H_2S+Na_2SO_3$. D. Vanino, and O. Schmidt studied the compounds of thiosulphuric acid with the aldehydes: $H_2S_2O_3+CH_2O\rightleftharpoons HO.CH_2.HS_2O_3$; etc. O. Y. Magidson and V. M. Krol prepared *sodium ethylene thiosulphate,* $Na_2C_2H_4(S_2O_3)_2$.

Sodium thiosulphate in most of its reactions in the absence of air and of oxidizing agents is resolved into a mixture of sulphite and sulphur; in acidic soln., hydrogen sulphide may be given off. The facility with which the thiosulphates form metal sulphides led C. Himly[10] and J. Landauer to propose its use as a group reagent in place of hydrogen sulphide when the metal sulphide and sodium sulphite are formed. F. Muck said that sodium decomposes thiosulphate into sulphite and sulphide. W. Spring observed that **sodium amalgam** reduces a soln. of alkali thiosulphate to a mixture of sodium sulphite and sulphide: $Na_2S_2O_3+2Na=Na_2S+Na_2SO_3$. E. Priwoznik said that **copper** is blackened in a few weeks by a soln. of sodium thiosulphate; and finely divided copper with a boiling soln. forms a precipitate of copper sulphide and a soln. of sodium sulphite free from sulphide. A similar observation was made by F. J. Faktor, and V. Merz and W. Weith: $Na_2S_2O_3+2Cu=Cu_2S+Na_2SO_3$. E. Priwoznik said that when **silver** is boiled with a soln. of sodium thiosulphate it becomes coated with a film of silver sulphide. F. J. Faktor also observed the blackening of silver by soln. of the thiosulphate. A. Mathieu-Plessy found that when an acetic acid soln. of sodium thiosulphate is warmed with **magnesium,** hydrogen, and hydrogen sulphide and sulphur are formed. F. J. Faktor represented the reaction with magnesium and a boiling soln. of the thiosulphate: $Mg+2H_2O=Mg(OH)_2+H_2$; $Na_2S_2O_3+H_2=H_2S+Na_2SO_3$; $Mg(OH)_2+2H_2S=Mg(SH)_2+2H_2O$. Anhydrous sodium thiosulphate with one-fifth its weight of magnesium powder, heated to redness, furnishes magnesium sulphide and sulphate. P. Neogi and R. C. Bhattacharyya found that thiosulphates are reduced to sulphite and sulphide by magnesium amalgam. H. Vohl observed that a hydrochloric acid soln. with **zinc** gives off hydrogen sulphide, and J. Reynolds said that the reaction enables one part of the thiosulphate in 500,000 parts of soln. to be detected. F. J. Faktor found that **cadmium** is coloured yellow by a hot soln. of sodium thiosulphate. L. L. de Koninck represented the reaction with **aluminium** in the presence of alkali-lye: $Na_2S_2O_3+2NaOH+2H=Na_2SO_3+Na_2S+2H_2O$. E. Priwoznik found that **tin** becomes coated with the sulphide. F. J. Faktor observed that when heated with anhydrous sodium thiosulphate, tin furnishes the sulphide, that with a soln. of sodium thiosulphate, **lead** gives a film of black sulphide; **bismuth**, brownish-black bismuth trisulphide, the lead-bismuth alloys, both lead and bismuth sulphides; and powdered **iron,** a black sulphide. When the anhydrous thiosulphate is heated to redness with one-fifth its weight of iron, dark green, needle-like crystals of $Na.FeS_2$ are formed; and at a lower temp., brownish-black powder is produced. J. de Girard obtained surface colours on the metals by treating them with double thiosulphates.

A. Geuther [11] found that **silver oxide** does not simply exchange its oxygen atom for a sulphur atom of sodium thiosulphate, but undergoes a reaction occupying three stages: $Na_2S_2O_3+Ag_2O=Ag_2S_2O_3+Na_2O$; $Ag_2S_2O_3=Ag_2S+SO_3$; and $SO_3+Na_2O=Na_2SO_4$. Hence he inferred that the thiosulphates are not simply sulphates with an oxygen replaced by sulphur. F. J. Faktor strongly heated a mixture of **zinc oxide** with five times its weight of anhydrous sodium thiosulphate and found that sulphur dioxide is given off and zinc sulphide formed. F. J. Faktor said that black mercuric sulphide is produced when mercuric oxide is warmed with a soln. of sodium thiosulphate. When anhydrous sodium thiosulphate is warmed with one-fourth its weight of **alumina,** aluminium sulphide is produced. R. F. Weinland and A. Gutmann found that sodium thiosulphate gives a precipitate of stannous sulphide when treated with **sodium stannite;** the mother liquor contains sodium sulphite and stannate; **potassium stannite** behaves similarly; while **sodium plumbite** is without action at ordinary temp., and when heated on a water-bath forms a small quantity of lead oxide and sulphide, while most of the sodium thiosulphate remains unaltered in soln. J. W. Slater found that a soln. of **chromic acid** gives, when boiled with sodium thiosulphate, a precipitate of chromic oxide. J. Myers said that the reaction with chromic acid soln. at ordinary temp. is a scarcely perceptible precipitate which when heated becomes brown under conditions where a pentathionate would remain clear. T. Diehl represented the reaction: $8H_2CrO_4+3H_2S_2O_3+7H_2O=6H_2SO_4+8Cr(OH)_3$; and A. Longi said that the main reaction is $2H_2CrO_4+6H_2S_2O_3=3H_2S_4O_6+2Cr(OH)_3+2H_2O$; and there is a secondary reaction $14H_2CrO_4+3H_2S_4O_6+16H_2O=12H_2SO_4+14Cr(OH)_3$. Both the thiosulphate and tetrathionate in the presence of hydrochloric or sulphuric acid or chromic salts develop hydrogen sulphide. J. W. Slater, and A. Longi said that in the absence of acids, **potassium dichromate** is very little if at all decomposed. G. Grather and T. Nagahama studied the reduction of dichromates by the thiosulphate. According to F. J. Faktor, in the presence of hydrogen dioxide, chromates form chromic hydroxide and chromic salts. A soln. of sodium thiosulphate dissolves **thallous dichromate,** forming yellow thallous chromate, and when the liquid is heated with ammonium chloride, chromic hydroxide is precipitated. When **sodium chromate** is heated with four times its weight of anhydrous sodium thiosulphate, a sulphate and sulphide are produced as well as a complex sulphide $NaCrS_2$. A soln. of sodium thiosulphate reduces **ammonium molybdate** to molybdenum dioxide; and **sodium tungstate** forms tungsten dioxide and heptoxide. When anhydrous sodium thiosulphate is heated with one-fourth its weight of **molybdenum trioxide,** molybdenum disulphide is formed, and with **tungsten trioxide,** tungsten disulphide. J. Stingl and T. Morawsky said that **potassium permanganate** can oxidize sodium thiosulphate in neutral soln., forming $KH_3Mn_4O_{10}$, while M. Hönig and E. Zatzek said that this oxidation can take place only in alkaline soln. forming $KH_3Mn_3O_8$; and I. M. Kolthoff said that the reaction is complete with a large excess of permanganate in alkaline soln., in acidic or neutral soln., the reaction with a large excess of permanganate was incomplete even after 24 hrs. M. Gläser said that the alkalinity produced by potassium carbonate in M. Hönig and E. Zatzek's experiments plays no part in the reaction, and that sodium thiosulphate can be completely oxidized in neutral soln.: $3Na_2S_2O_3+8KMnO_4+3H_2O=2KH_3Mn_4O_{10}+3Na_2SO_4+3K_2SO_4$. To this M. Hönig and E. Zatzek replied that when neutral soln. are boiled with permanganate in excess, sulphur always remains in soln. after precipitating the sulphuric acid formed with barium chloride; this is oxidized to sulphuric acid on addition of bromine. When, on the other hand, an alkaline soln. of thiosulphate is boiled with excess of permanganate, the whole of the sulphur can be removed as barium sulphate, and no more sulphuric acid is obtained by adding bromine. They also conclude that the composition of the precipitated manganite cannot be relied on to indicate the nature of the decomposition, as the precipitate has no constant composition. G. Brügelmann used the process for the determination of thiosulphate, for with an excess of permanganate the thiosulphate is oxidized to sulphate: $2KMnO_4+Na_2S_2O_3=K_2SO_4+Na_2SO_4+Mn_2O_3$, and the dissolved sulphate is determined in the usual way. According to C. Luckow, a soln. of sodium thiosulphate, whether neutral, acidified by sulphuric acid, or made alkaline with potash-lye, when boiled with an excess of potassium permanganate, reduces only so much of the latter as corresponds with what is required by the equation $2H_2S_2O_3+7O+H_2O=2H_2SO_4+H_2S_2O_6$, and the dithionic acid can be detected in the oxidized soln. The reaction was also examined by H. Kiliani. F. Raschig said that in alkaline soln., permanganate oxidizes thiosulphate to sulphate. M. C. Lea found that **ruthenium trioxide,** Ru_2O_3, produces with hydrochloric acid and sodium thiosulphate when sat. with ammonia, a rose-red or carmine-red colour which is almost black in conc. soln. The reaction is sensitive to the presence of one part of sodium thiosulphate in 25,000 parts of liquid.

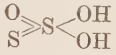
If an alkali thiosulphate be added to a soln. of a metal salt, there is formed a soluble or an insoluble metal thiosulphate, which may dissolve in an excess of the thiosulphate to form a complex salt. This soln. may be stable or unstable; some soln. decompose at ordinary temp., others require the application of more or less heat, and the metal sulphide is precipitated, while others again are stable when heated. When the soln. is acidified, the metal may be precipitated as sulphide. J. W. Slater said that all the metals precipitated by hydrogen sulphide in acidic soln. are precipitated from hot soln. of sodium thiosulphate by hydrogen sulphide. A. L. Orlowsky found that soln. of lead and cadmium behave rather differently. The alkaline earths are precipitated as thiosulphates from these soln. by the addition of ammonia, and they are converted into sulphates and sulphites when boiled for a long time. G. Vortmann showed that the behaviour of a boiling soln. of sodium thiosulphate, in neutral or feebly acidic soln., depends on the nature of the metal. If it does not form a sulphide in aq. soln., the hydroxide may be precipitated—*e.g.* aluminium; if it forms an insoluble sulphide, that will be precipitated and sulphuric acid formed—*e.g.* copper and silver; if the metal sulphide is readily reduced, or the thiosulphate is in great excess, reduction may occur and tetrathionic acid be formed—*e.g.* cupric to cuprous salts; in some cases the metal sulphide is formed and sulphur dioxide evolved, some sulphuric and tetrathionic acids may be formed—*e.g.* arsenic, antimony, tin.

The behaviour of some salt soln. towards sodium thiosulphate is indicated in connection with the individual thiosulphates. The tendency of the thiosulphates to form complex salts is noteworthy. As noted by J. F. W. Herschel, the aq. soln. of the alkali thiosulphates dissolve many metal oxides and salts in consequence of the formation of soluble complex salts; and hence the application of thiosulphates in photography, and their use in the extraction of silver from its ores—**3.** 22, 3. The action of the thiosulphates on **copper, and silver salts** is discussed in connection with their thiosulphates. E. Müller studied the electrometric titration of thiosulphate and silver nitrate. H. Bassett and R. G. Durrant found that when copper salts in presence of excess of thiosulphates are heated with mineral acids, cuprous sulphide is precipitated, but this precipitation is not complete even after prolonged boiling if hydrochloric acid is employed. The reason for this appears to depend on the formation of the double chloride mentioned above, which cannot decompose into cuprous sulphide. The precipitation is complete if nitric acid is used, provided the conc. of the acid is less than $0 \cdot 5N$-, and is complete with sulphuric acid, which should be fairly concentrated if any copper chloride is present. In these circumstances, pentathionic acid is produced through the interaction of thiosulphate, tetrathionate, and mineral acid. J. T. Norton observed that between 140° and 200°, salts of silver and copper are completely precipitated as sulphides by sodium thiosulphate. According to J. Hanus and V. Hovorka, the precipitate formed in the reaction between cupric salts and sodium thiosulphate consists of a mixture of cuprous and cupric sulphides and varying proportions of free sulphur. The composition depends on the duration of boiling, the proportion of thiosulphate, and the acidity of the soln. The maximum amount of cuprous sulphide was obtained from soln. with 2·5 to 3·0 mols of thiosulphate per gram-atom of copper; increasing the thiosulphate decreased the proportion of cuprous sulphide until, with 15 to 30 mols per gram-atom of copper, the precipitate consisted largely of cupric sulphide and sulphur. The composition of the precipitate in acidic soln. containing 4 to 5 mols of thiosulphate per gram-atom of copper was $Cu_2S:CuS=8:92$ per cent. J. Bodnar based a method of determining thiosulphates in the presence of sulphites on the fact that the thiosulphate alone reduces silver nitrate to sulphide and sulphuric acid—the latter is determined with standard alkali in the filtered liquid. As shown by M. C. Lea, in the presence of free acids, silver and **gold salts** behave as they do towards hydrogen sulphide. F. J. Faktor found that when anhydrous sodium thiosulphate is heated with one-fourth its weight of copper chloride, some sulphur and sulphur dioxide are given off, and cuprous sulphide is formed; with silver nitrate, black silver sulphide is produced; and with **cadmium chloride,** cadmium sulphate and sulphide. J. T. Norton said that **beryllium salts** are imperfectly precipitated as hydroxide by sodium thiosulphate at 140°–200; and likewise cadmium and **zinc salts** are completely precipitated as sulphides by sodium thiosulphate; and **mercury salts** behave similarly. According to M. C. Lea, in acidic soln. mercury salts behave towards thiosulphates the same as they do towards hydrogen sulphide. H. W. F. Wackenroder and L. A. Buchner said that mercuric nitrate soln. give a lemon-yellow precipitate which with an excess of the nitrate becomes yellowish-white; and H. Rose, that mercuric salts, not in excess, produce a white precipitate of mercuric thiosulphate, which becomes yellow, brown, and finally black, owing to its passage into mercuric sulphide—the change is rapid with hot soln.; if mercuric salt be in excess, the white precipitate is not changed even on boiling, and it is said to be a compound of mercuric sulphide and thiosulphate. In both cases, the liquid contains sulphuric acid. F. Field said that an aq. soln. of mercurous iodide, and H. Fleck, a soln. of mercuric chloride in sodium thiosulphate, when warmed, give a precipitate of mercuric sulphide, while J. C. Schnauss observed that mercuric chloride does not furnish mercuric sulphide, but rather a complex salt, $NaHgS_2O_3$. W. Feld represented the reaction as an oxidation process: $Na_2S_2O_3+2HgCl_2+H_2O=Na_2SO_4+2HgCl+2HCl+S$, which is supported by the fact that the precipitate is white. A. Sander supported the older statements of J. F. W. Herschel, H. Rose, and F. Kessler, that the white precipitate is a chlorosulphide $Hg_3S_2Cl_2$. F. J. Faktor added that a warm soln. of mercurous chloride and sodium thiosulphate gives a black precipitate. F. J. Faktor represented the reaction with gold chloride, when warmed, by $2AuCl_3+6HgCl+3Na_2S_2O_3=6HgCl_2+Au_2S_3+3Na_2SO_3$. When red mercuric sulphide is digested with a soln. of sodium thiosulphate it takes on a fiery red colour. If anhydrous sodium thiosulphate be warmed with one-fourth its weight of mercuric chloride, black mercuric sulphide is formed. G. Vortmann also noted the formation of sulphide, sulphuric acid, traces of tetrathionic acid, and no pentathionic acid when mercuric salts are treated with sodium thiosulphate. J. T. Norton showed that **salts of aluminium, chromium, titanium, zirconium, and thorium** are completely precipitated as hydroxides when treated with soln. of sodium thiosulphate at 140°–200°; and that whilst aluminium and chromium salts are not completely precipitated by boiling during a "reasonable" time under atm. press., they are quantitatively precipitated under 20 atm. press. Zirconium and titanium hydroxides are precipitated quantitatively by boiling a few minutes at atm. press. F. L. Hahn studied the reaction with aluminium salts. F. J. Faktor found that alkaline soln. of **thallous salts** form a white precipitate with sodium thiosulphate, and this becomes brown when boiled, and brownish-black thallous sulphide is produced if hydrochloric, sulphuric, or acetic acid be present; hot soln. of thallous salts and sodium thiosulphate form a brown liquid; thallous chloride is easily soluble in sodium thiosulphate soln., thallous bromide is sparingly soluble, and thallous iodide is virtually insoluble. A. Benrath and K. Ruland found that **ceric sulphate** converts sodium thiosulphate into tetrathionate: $2Na_2S_2O_3+2Ce(SO_4)_2 = Ce_2(SO_4)_3+Na_2SO_4+Na_2S_4O_6$. Anhydrous sodium thiosulphate heated with one-fourth its weight of thallous sulphate formed thallium sulphide, Tl_4S_5; similarly, **stannous chloride** reacts: $6Na_2S_2O_3+2SnCl_2=3Na_2SO_4+2SnS+Na_2S+4NaCl +3S+3SO_2$; and **lead chloride** forms lead sulphide—*vide infra*, lead and tin thiosulphates—**bismuth chloride,** the complex sulphide $NaBiS_2$. J. T. Norton found that lead salts are completely precipitated as sulphide when treated with a soln. of sodium thiosulphate at 140° to 200°; and he also found that at 140° to 200°, manganese is only incompletely precipitated as sulphide from soln. of **manganese salts.** According to F. J. Faktor, when anhydrous sodium thiosulphate is heated with one-fourth its weight of manganese chloride, there is formed the complex sulphide $Na_2Mn_3S_4$; with **cobalt chloride,** $Na_2Co_4S_6$; and with **nickel chloride,** $Na_2Ni_2S_3$. In the presence of hydrogen dioxide, soln. of manganese salts with sodium thiosulphate give a brown precipitate of hydroxide; cobalt salts a black, and nickel salts a pale green precipitate. According to H. Schiff, and A. Lenz, **ferric salts,** in the cold, form with sodium thiosulphate violet or reddish-black coloured soln., which probably contain an unstable ferric thiosulphate, which, according to J. P. Claësson, becomes dark red when treated with ammonia. After standing some time, the soln. becomes colourless owing to a reaction which O. Popp, and K. Jellinek and L. Winogradoff symbolized: $2Na_2S_2O_3 + 2FeCl_3=2NaCl + 2FeCl_2 + Na_2S_4O_6$—*vide infra*, ferric thiosulphate. The reaction was studied by A. von Kiss. J. T. Hewitt and G. R. Mann observed that the reduction of ammonium ferric alum, $2Fe'''+2S_2O_3''=2Fe''+S_4O_6''$, is a quadrimolecular reaction, and probably two complexes containing iron react with two thiosulphate molecules. J. Holluta and A. Martini found that the initial acceleration of the reaction cannot be ascribed to the autocatalytic action of the end-product—the ferrous or tetrathionate ions; to the catalytic action of the sulphur formed in the reaction; or to the means adopted to stop the reaction at the required point. J. T. Norton found that salts of iron, cobalt, and nickel are completely precipitated as sulphides when treated with a soln. of sodium thiosulphate at 140°–200°. E. Pietsch and co-workers studied the surface conditions in the reaction with ferric chloride. M. C. Lea found that soln. of **platinum salts,** in the presence of free acid, behave towards sodium thiosulphate as they do with hydrogen sulphide.

The constitution of the thiosulphates.—In 1855, W. Odling[12] suggested that thiosulphuric acid be regarded as sulphuric acid with one atom of oxygen replaced by sulphur so that sulphurous, thiosulphuric, and sulphuric acids were respectively related as $H.SO_2.OH$, $HS.SO_2.OH$, and $HO.SO_2.OH$, and that the oxidation of sulphurous acid furnishes sulphuric acid, and the sulphurization of sulphurous acid, thiosulphuric acid. This agrees with C. J. Koene's view, who also assumed that the anhydride is to be regarded as sulphur trioxide with one atom of oxygen replaced by one of sulphur. E. Mathieu-Plessy said that the alkaline thiosulphates in the presence of acetic acid have a stability sufficient to render them analogous to the corresponding sulphates. G. G. Stokes found that as a rule the halides of quinine, or those salts in which quinine is not directly combined with oxygen, do not manifest fluorescence, whereas the oxygen salts, like sulphates and nitrates, are fluorescent. The thiosulphates are exceptional in being non-fluorescent. H. Rose thought that all thiosulphates contain hydrogen, and the formula

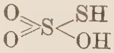
$H_2S_2O_3.H_2O$, or H_2SO_2, was suggested for the thiosulphuric acid, which was thus related more to sulphurous than to sulphuric acid: $H.SO_2.H$ representing thiosulphuric acid; $H.SO_2.OH$, sulphurous acid; and $HO.SO_2.OH$, sulphuric acid. C. Pape, however, prepared anhydrous thiosulphates of potassium, sodium, barium, and lead, so that this argument lost weight. A. Dupré, however, supported the argument from his observations on the synthesis of formic and thiosulphuric acid, suggesting that thiosulphuric acid resembles formic acid, $H.CO_2H$, by having the carbon replaced by sulphur; and W. Odling also emphasized the relation by comparing the reduction of carbonic acid to formic acid: $H_2CO_3+2Na=H.CO_2Na+NaOH$, with the reduction of sulphurous acid to thiosulphuric acid: $H_2SO_3+2Na=H.SO_2Na+NaOH$. The tendency of the thiosulphates to split up so as to give an atom of free sulphur: $Na_2S_2O_3+2HCl=2NaCl+H_2O+SO_2+S$, can be explained also by the alternative formula $2NaHSO_2+2HCl=2NaCl+2H_2O$ SO_2+S. The tendency of a thiosulphate to furnish a sulphate and sulphide is parallel to the tendency of a hypophosphite or phosphite to furnish a phosphate and phosphide.

C. Schorlemmer preferred W. Odling's original formula $HO.SO_2.SH$, and C. W. Blomstrand held that thiosulphuric acid may have the constitution $HO.S(S)O.OH$, although the preparation of toluyl thiosulphate from potassium hydrosulphide: $C_7H_7SO_2Cl+2KSH=KCl+H_2S+C_7H_7SO_2.SK$, is in agreement with the formula $HO.SO_2.SH$. J. Y. Buchanan also said that the action of phosphorus pentachloride on lead thiosulphate does not yield sulphuryl chloride as would be anticipated if the formula of the acid were $HS.SO._2OH$. M. Picon also recommended the formula $S=SO<\begin{smallmatrix}OH\\OH\end{smallmatrix}$. W. Spring supposed that the two sulphur atoms in thiosulphuric acid are bivalent, and based his inference on the reactions: $C_6H_5SO_2.Cl+K_2S=KCl+S+C_6H_5SO_2K$; and $C_6H_5SO_2K+S=C_6H_5S_2O_2K$, and on the assumption that the HSO_3-radicle is concerned in these reactions. W. Spring's formula is $H.S.S.O.O.O.K$. This does not conflict with J. Y. Buchanan's experiment. A. Michaelis held that thiosulphuric acid is not related to sulphurous or sulphuric acid because of the formation of ammonium thiosulphate from ammonium sulphate and phosphorus pentasulphide. D. I. Mendeléeff represented thiosulphuric acid as a derivative of hydrogen sulphide containing the univalent HSO_3-radicle in place of hydrogen $H—S—HSO_3$. This is another way of representing the formula $HS.SO_2OH$. The rival formulæ for thiosulphuric acid are:



$$\begin{smallmatrix}O\\S\end{smallmatrix}\!\!>S<\!\!\begin{smallmatrix}OH\\OH\end{smallmatrix}$$

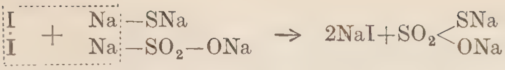
Symmetrical.



$$\begin{smallmatrix}O\\O\end{smallmatrix}\!\!>S<\!\!\begin{smallmatrix}SH\\OH\end{smallmatrix}$$

Asymmetrical.

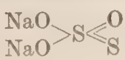
and E. Drechsel held that both forms can exist as isomers. As a rule, phosphorus sulphide acts on many compounds, replacing oxygen by sulphur, and generally, the oxygen atoms in hydroxyl groups are more susceptible to sulphurization than oxygen atoms directly united to sulphur. The formation of thiosulphates by the action of phosphorus sulphide on sulphates is taken to favour the $HS.SO_2.OH$ formula. A similar conclusion follows from the formation of thiosulphates by the action of hydrogen sulphide on sulphur trioxide: $H_2S+SO_3=HS.SO_2.OH$, analogous with the action of water on the trioxide $H_2O+SO_3=HO.SO_2.OH$. Again, sodium thiosulphate is formed when a mixture of sodium sulphide and sulphite is treated with iodine: $Na_2S+Na_2SO_3+I_2=Na_2S_2O_3+2NaI$. This reaction can be supposed to occur in two steps: $Na_2S+I_2=2NaI+S$; and the liberated sulphur acts upon the sodium sulphite as previously indicated or else the iodine can be supposed to withdraw one atom of sodium from a mol of sodium sulphide and one from the mol of sodium sulphite, and the residues to unite to form a more complex mol—a condensation product. This operation, sometimes called **Spring's reaction**—after W. Spring's syntheses of the thionic acids by a similar reaction in 1874—is symbolized:



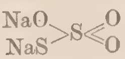
$$\begin{array}{l} I \\ I \end{array} + \begin{array}{l} Na-SNa \\ Na-SO_2-ONa \end{array} \rightarrow 2NaI+SO_2<\begin{array}{l} SNa \\ ONa \end{array}$$

H. Bassett and R. G. Durrant suggested that the reaction is not termolecular, but rather involves the two-stage reaction in which the complex $Na_2S_2O_3.I_2$ is first formed, and this reacts with another mol of thiosulphate to form the tetrathionate. In support of the asymmetrical formula, H. Bunte found that ethyl thiosulphate can be prepared from ethyl bromide and sodium thiosulphate: $NaS.SO_2.ONa+C_2H_5Br=NaBr+C_2H_5S.SO_2.ONa$, which, with hydrochloric acid, yields mercaptan, $C_2H_4.SH$, and sulphuric acid: $NaO.SO_2.SC_2H_5+H_2O=NaO.SO_2.OH+C_2H_5SH$. This is taken to prove that the ethyl radicle is in direct combination with sulphur. In support of this, H. Schwicker reported that the isomeric salts, $KS.SO_2.ONa$ and $NaS.SO_2.OK$, can be prepared—by the action of ammonium sulphide on the two sulphites, $K.SO_2.ONa$ and $Na.SO_2.OK$. This argument, however, has little weight because of the doubts as to the existence of the isomeric sulphites (*q.v.*). On the other hand, the asymmetric formula is supported by the electrolytic reduction of sodium benzyl thiosulphate, $Na(C_6H_5.CH_2)S_2O_3$, which was observed by T. S. Price and D. F. Twiss to form dibenzyl disulphide, $(C_6H_5.CH_2)_2S_2$, presumably by the reaction: $2(C_7H_7S.SO_2.ONa)+H_2=2NaHSO_3+(C_7H_7)_2S_2$. A. Gutmann favoured the symmetrical formula from his study of the action of sodium hydroxide, sodium arsenite, and of potassium cyanide on the tri- and tetra-thionates. He found that when sodium tetrathionate reacts with sodium arsenite in alkaline soln., two mols of monosulphoxyarsenate, one of arsenate, and two of sulphite are formed: $Na_2S_4O_6+3Na_3AsO_3+2NaOH=2Na_3AsSO_3+Na_3AsO_4+2Na_2SO_3+H_2O$; that is, $S_4O_5=2S+O+2SO_2$. This, he said, cannot be explained by D. I. Mendeléeff's formula for the tetrathionate, derived from the asymmetrical formula $NaS.SO_2.ONa$ for the thiosulphate; but with the symmetrical formula NaO.SOS.ONa, the formula for the tetrathionate becomes NaO.SOS.O.O.SOS.ONa, a derivative of persulphuric acid. The reaction with sodium arsenite then becomes $NaO.SOS.O.O.SOS.ONa \rightarrow NaO.SO.O.SO.ONa+O+2S$; corresponding conversion of the persulphate into pyrosulphate: $NaO.SO_2.O.O.SO_2ONa \rightarrow NaO.SO_2.O.SO_2.ONa+O$. This all means that the two $SO_2.ONa'$-residues left after withdrawing two atoms of sulphur from a mol of the tetrathionate built on D. I. Mendeléeff's scheme should unite and form a mol of dithionate, and the dithionate would not then give arsenate and sulphate since dithionates have no action on arsenites. A. Friessner showed that when neutral or alkaline soln. of sodium sulphite are electrolyzed the process is represented: $2SO_3''+O+H_2O=S_2O_6''+2OH'$ and not $2SO_3''+2\oplus=S_2O_6''$, meaning that sulphite ions do not condense to form dithionate ions. Hence, argue T. S. Price and D. F. Twiss, the two $SO_2.ONa'$-residues may not unite to form dithionate, but rather react: $2(SO_2.ONa)+2NaOH=2Na_2SO_3+H_2O+O$, and A. Gutmann's argument loses its cogency in favour of the symmetrical formula for the thiosulphates—*vide infra*, polythionic acids. H. Debus explained the constitution of the polythionic acids (*q.v.*) by assuming that the sulphur enters the molecule of sulphurous acid through the $H.SO_2$-radicle to form the $KS.SO_2$-radicle. Some thiosulphates—*e.g.* that of calcium—easily lose sulphur and become sulphite, indicating that the second atom of sulphur is held in the mol of thiosulphate by a feeble force. H. Burgarth discussed the electronic structure.

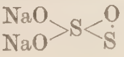
As a matter of fact, many reactions of the thiosulphates can be grouped in favour of the symmetrical formula and yet others in favour of the asymmetrical formula. It can also be assumed, as in the case of the sulphites, etc., that a tautomeric change is involved, $NaO.SO_2.SNa \rightleftharpoons NaO.SOS.ONa$. It is generally supposed, as in the case of the sulphates, that the central sulphur atom is sexivalent, although it can be argued in both cases that the central sulphur atom is quadrivalent:



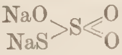
$$\begin{array}{l} NaO \\ NaO \end{array}>S\leqslant\begin{array}{l} O \\ S \end{array}$$



$$\begin{array}{l} NaO \\ NaS \end{array}>S\leqslant\begin{array}{l} O \\ O \end{array}$$



$$\begin{array}{l} NaO \\ NaO \end{array}>S<\begin{array}{l} O \\ S \end{array}$$



$$\begin{array}{l} NaO \\ NaS \end{array}>S\leqslant\begin{array}{l} O \\ O \end{array}$$

The dibasicity of the acid agrees with A. F. Hollemann's observations on the electrical conductivity of sodium thiosulphate. P. Walden compared the electrical conductivities of soln. of magnesium sulphate and thiosulphate, and found that the latter has slightly the greater conductivity in agreement with the assumption that the formula of the acid is $HO.SO_2.SH$, because sulphur is more electronegative than oxygen, and therefore forms better conducting salts. K. Barth considered that the electrical conductivity of soln. of silver sodium thiosulphate, $Ag_2S_2O_3.2Na_2S_2O_3$ or $Na_4Ag_2(S_2O_3)_3$, favoured the assumption that the complex is the sodium salt, $Na_3(NaAg_2S_6O_3)$, of a tribasic acid, $H_3(NaAg_2S_6O_9)$. For the co-ordination formula, *vide* the polythionates. The conception of the acid $H_2S_2O_3$ as thiosulphuric acid, $OH.SO_2.SH$, implies that it is a mixed anhydride of sulphuric acid and hydrogen sulphide, just as chlorosulphonic acid is a mixed anhydride of sulphuric and hydrochloric acids. Its properties do not agree with this conception, for it decomposes, not into sulphuric acid and hydrogen sulphide, but into sulphurous acid and sulphur in aq. soln. J. Piccard and E. Thomas showed that at the temp. of liquid air, in carbon dioxide soln., sulphur trioxide and hydrogen sulphide combine to give what is presumed to be the true thiosulphuric acid. In this compound, the sulphur takes the place of negative, bivalent oxygen in sulphuric acid. Ordinary thiosulphuric acid must be an electronic isomeride of the true thiosulphuric acid, the additional sulphur atom being neutral. In the true thiosulphuric acid, the central sulphur atom is sexivalent; in the isomeride it is quadrivalent. The difference can be expressed only by the co-ordination formulæ thus:

$$\left[\begin{array}{ccc} S^{O} & & -O^{II} \\ & +S^{IV} & \\ -O^{II} & & -O^{II} \end{array}\right]\begin{array}{l} H+ \\ H+ \end{array} \qquad \left[\begin{array}{ccc} -S^{II} & & -O^{II} \\ & +S_{VI} & \\ -O^{II} & & -O^{II} \end{array}\right]\begin{array}{l} H+ \\ H+ \end{array}$$

Some reactions of analytical interest.—In qualitative analysis the thiosulphates can be recognized by the precipitation of sulphur with the evolution of sulphur dioxide when their soln. are treated with **acids**—hydrochloric, acetic, etc. O. Hackl[13] said that the reaction is not very sensitive, for the sulphur separation occurs in the cold only in 5 mins. with 100 c.c. of a soln. containing a miligram of thiosulphate per c.c. Sulphides in the presence of oxidizing agents may give similar reactions owing to their conversion into thiosulphates. These salts also give distinctive reactions as a result of their great reducing power, *e.g.* the violet coloration with **ferric chloride** which is not exhibited by sulphites; and the decolorization of permanganate or iodine soln. M. E. Pozzi-Escot recommended the following test for thiosulphates: Add to one c.c. of the test soln. an equal vol. of a 10 per cent. soln. of **ammonium molybdate,** and run in gently some conc. sulphuric acid so as to form a layer on the bottom. If thiosulphates be present, a blue layer is formed at the junction of the two soln. The reaction is due to the reducing action of thiosulphuric acid which is set free in dil. soln., but in more conc. soln. is split into sulphurous acid and hydrogen sulphide. 0·00005 grm. of sodium thiosulphate in one c.c. of soln. can be detected in this way. **Silver salts** give a white precipitate of silver thiosulphate which soon turns yellow, then brown, and black owing to the formation of silver sulphide; the white precipitate is soluble in an excess of the thiosulphate, and also in nitric acid. O. Hackl said that the reaction with silver nitrate will detect 1 mgrm. of S_2O_3'' in 100 c.c. of water. **Barium salts** give a white crystalline precipitate sparingly soluble in cold water, but soluble in nitric acid; **strontium salts** give no precipitate, and in this respect can be distinguished from the sulphites. **Calcium salts** do not give a precipitate unless in conc. soln. **Mercuric chloride** produces a bluish-black opalescence with trace of thiosulphate, larger amounts give a white precipitate of calomel. The mercuric chloride soln. is usually mixed with ammonium chloride since the resulting double chloride $HgCl_2(NH_4Cl)_2$ is more sensitive than mercuric chloride alone. The soln. is also usually acidified with hydrochloric acid to prevent the precipitation of mercuric carbonate should the water contain traces of carbonates in soln. Unlike soln. of the sulphides, the thiosulphates give no precipitate with zinc or manganese salts. The formation of hydrogen sulphide with zinc and an acid is characteristic. Unlike the sulphites, the thiosulphates give no red colour with **zinc sulphate and sodium nitroprusside**; but the thiosulphates give a violet colour with sodium nitroprusside after being reduced with aluminium and potassium hydroxide. According to L. L. de Koninck, thiosulphates behave like sulphites towards zinc or aluminium and hydrochloric acid, but with aluminium in a soln. of alkali hydroxide, thiosulphates, not sulphites, give a soln. of alkali sulphide; sodium amalgam also reduces thiosulphates to sulphides, but not so with the sulphites. H. von Pechmann and P. Manck showed that if a thiosulphate be heated with **potassium cyanide,** a sulphite and thiocyanate are formed. The latter will give the characteristic reaction with ferric chloride.

A mixture of thiosulphate, sulphate, sulphite, and sulphide can be treated by adding zinc chloride so as to precipitate zinc sulphide. This is filtered off, and barium chloride added to the soln. along with ammonium chloride and hydrochloric acid; the barium sulphate is removed by filtration, and iodine is added to convert the sulphite into sulphate and tetrathionate; again, barium chloride is added, and the filtrate from the barium sulphate is treated with bromine to oxidize the tetrathionate to sulphate, which can be then precipitated in the usual way.

Thiosulphates can be determined gravimetrically by oxidizing them to sulphates with **bromine,** and subsequently precipitating the sulphur as barium sulphate. The warming of the soln. with an excess of silver nitrate results in the precipitation of half the silver as sulphide which can be weighed as Ag_2S or in some other form. Thiosulphates can be determined volumetrically by titration with **iodine**: $2Na_2S_2O_3+I_2=Na_2S_4O_6+2NaI$ or by S. Eliasberg's process, for when neutral **hydrogen dioxide** is added to neutral sodium thiosulphate along with a definite volume of standard potassium hydroxide, the reaction $Na_2S_2O_3+4H_2O_2+nKOH\rightarrow Na_2SO_4+K_2SO_4+5H_2O+(n-2)KOH$ occurs. The excess of potassium hydroxide can be determined in the usual manner.

According to E. Pittarelli, thiosulphuric and sulphurous acids in an organic liquid may be distinguished by addition ot aurine, coralline, or rosolic acid strongly acidified with hydrochloric acid, the presence of sulphurous acid being indicated by instantaneous decolorization; if this occurs, addition of aurine is continued until the liquid is saturated with it and becomes distinctly yellow. If this colour persists for 24 hrs., only sulphite is present, but if the liquid undergoes decolorization, it contains thiosulphate. The sensitiveness of this reaction, which is not shown in presence of hydrogen sulphide, is 1 : 500,000. J. Reynolds gave for the sensitiveness of the nitroprusside tests 1 : 6000; the ferric chloride test, 1 : 30,000; the iodine and starch test, 1 : 160,000; the ferric chloride and ferrocyanide test, 1 : 300,000; and the zinc and acid test, with lead-test paper, 1 : 300,000. According to E. H. Riesenfeld and E. Grünthal, on adding copper sulphate to sodium thiosulphate soln., in neutral soln. a yellow precipitate and in hydrochloric acid soln. a white precipitate of a sodium cuprous thiosulphate of varying composition is obtained. The precipitate decomposes on keeping to form copper sulphide. In the absence of sulphides this reaction affords an excellent qualitative test for the detection of thiosulphates, being about ten times as sensitive as the usual hydrochloric acid reaction. Polythionates do not give this reaction.

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§ 38. The Thiosulphates

According to C. F. Rammelsberg,[1] and E. Divers and M. Ogawa, when a soln. of calcium thiosulphate—obtained by boiling lime and sulphur together with water, and leaving the soln. until much of the pentasulphide has oxidized—is treated with an excess of ammonium carbonate, filtered, and freely exposed to air for some time at 50°–60°, a conc. soln. of ammonium thiosulphate is obtained, free from sulphate, and other salts. C. F. Rammelsberg said that when evaporated to dryness over sulphuric acid, rhombic plates of tritahydrated **ammonium thio-**

sulphate, $(NH_4)_2S_2O_3.\frac{1}{3}H_2O$, are formed; J. F. W. Herschel, and W. C. Zeise also made this salt. There is, however, some doubt about the existence of this hydrate, because, when a soln. of the salt is evaporated in a desiccator, A. Fock and K. Klüss, A. E. Arppe, and E. Divers and M. Ogawa obtained only the anhydrous salt. A. Fock and K. Klüss obtained the salt by treating a soln. of ammonium polysulphide with sulphur dioxide, and evaporating the clear soln. over sulphuric acid. A. E. Arppe obtained it as a by-product in the preparation of *p*-nitroaniline. W. Spring found that the anhydrous salt is sublimed from a heated mixture of ammonium sulphate and phosphorus pentasulphide. The product is contaminated with some ammonium polysulphide. Ammonium thiosulphate is not formed when sulphur trioxide, hydrogen sulphide, and ammonia are mixed together, but it is formed if ammonia and sulphur trioxide are united to form ammonium amidosulphonate, $NH_4SO_3(NH_2)$, and this treated with hydrogen sulphide to form ammonium thiosulphate. For other modes of formation, *vide supra*, the preparation of thiosulphuric acid. The tabular crystals were found by A. Fock and K. Klüss not to be isomorphous with the potassium salt, and to belong to the monoclinic system, having the axial ratios $a:b:c=1\cdot5677:1:1\cdot3575$, and $\beta=85°\ 26'$; G. Wyrouboff gave $1\cdot5717:1:1\cdot3500$, and $\beta=85°\ 25'$. The basal cleavage is perfect. C. F. Rammelsberg found that when the salt is heated, it furnishes water and ammonia, and a sublimate of sulphur, much ammonium thiosulphate, and some ammonium sulphite. W. Spring found that the dry salt can be sublimed with an intermediate dissociation. E. Divers and M. Ogawa found that the salt decomposes very slowly at 150°, the main products being a sublimate of anhydrous normal sulphite and a residue of unfused sulphur, as in the case of the trithionate. Very small quantities of hydrogen sulphide and ammonia also pass off in the current of nitrogen, and the sublimate contains a very little of a salt which has some of the properties of trithionate, and does not give the characteristic violet coloration with ferric chloride. The main reaction in the decomposition of the thiosulphate is in full agreement with the relation of thiosulphates to sulphites. Very interesting is the production of a little ammonia and hydrogen sulphide, in connection with the relation of trithionate to thiosulphate as its thioanhydride (Spring): $2(NH_4)_2S_2O_3=2NH_3+H_2S+(NH_4)_2S_3O_6$. When ammonium thiosulphate is rapidly and more strongly heated, ammonia is lost, and sulphur sublimes; then, as a matter of course, and of no significance, thiosulphate and even trithionate are produced on adding water to the mixed sublimates. The action of sulphur dioxide was discussed by W. Feld, and F. Overdick—*vide supra*. According to P. Pierron, when ammonium thiosulphate is electrolyzed in a compartment cell, with a platinum cathode and lead anode, below 15°, ammonium sulphide is the only product obtained at the cathode, whilst at the anode, sulphur with various proportions of sulphurous, sulphuric, trithionic, and tetrathionic acids is formed. The amounts of sulphur and sulphuric acid increase, whilst that of tetrathionic acid decreases as the current density rises from 10 to 40 amps. per sq. dcm. E. Divers and M. Ogawa found that ammonium thiosulphate is freely soluble in water; H. Stamm found its solubility is small in aq. ammonia; and A. Naumann, and W. Eidmann, that it is sparingly soluble in acetone. The use of ammonium thiosulphate in analytical work has been discussed by A. Carnot, and A. L. Orlowsky. A. Ferranti made a soln. of **hydrazine thiosulphate,** $(N_2H_4)_2H_2S_2O_3$, by adding barium thiosulphate to a soln. of hydrazine sulphate until the filtered liquid gives no further precipitate with barium chloride.

A. Fock and K. Klüss prepared **lithium thiosulphate,** $Li_2S_2O_3.3H_2O$, by double decomposition with soln. of lithium sulphate and barium thiosulphate; and evaporating the clear liquid over sulphuric acid. The colourless, deliquescent needles give off water and sulphur when heated, leaving a residue of lithium sulphate and sulphide. J. Meyer and H. Eggeling obtained the salt from soln. of lithium carbonate and barium thiosulphate. The hygroscopic salt is soluble in absolute alcohol.

F. Chaussier[2] prepared **sodium thiosulphate,** $Na_2S_2O_3$—which he called *hydrosulfure sulfuré de soude*—from sulphurous acid and sodium sulphide, or from sodium sulphite and hydrogen sulphide. L. N. Vauquelin prepared what he called *sulfites sulfurés,* by digesting soln. of sodium sulphate or sulphite with sulphur; and J. F. W. Herschel—following J. L. Gay Lussac—called the salt hyposulphite of soda, and obtained it by oxidizing a soln. of calcium hydrosulphide in air, and subsequent double decomposition with a sodium salt. The salt is produced by the action of sulphur on the alkali hydroxide or carbonate, or by the action of sulphur on the hydroxides or carbonates of the alkaline earths and subsequently transforming, say, calcium thiosulphate into the sodium salt by double decomposition with alkali sulphate, and crystallization. M. J. Fordos and A. Gélis showed that rather more thiosulphate is formed than corresponds with the reaction: $3Na_2O+nS+H_2O=2Na_2S_{n-2}+Na_2S_2O_3+H_2O$. J. B. Senderens said that this reaction applies only to a limiting state when the soln. are sufficiently concentrated to allow the formation of a high polysulphide; with dil. soln., the polysulphide forms thiosulphate and hydrogen sulphide. The reaction with alkali carbonate can be symbolized: $3Na_2CO_3+8S=Na_2S_2O_3+2Na_2S_3+3CO_2$; and with milk of lime: $Ca(OH)_2+S=CaS+H_2O+O$; $CaS+3O=CaSO_3$; $CaSO_3+S=CaS_2O_3$; and $CaS+4S=CaS_5$. H. Pomeranz supposed that the reaction results in the formation of a sulphoxylate: $4NaOH+2S=Na_2S+Na_2SO_2+2H_2O$; or $3NaOH+2S=Na_2S+NaHSO_2+H_2O$. C. Fahlberg and M. W. Iles said that the molten alkali hydroxide, if not in excess, reacts with sulphur to form polysulphide and thiosulphate, but if not in excess, alkali sulphite and sulphate. E. Filhol and J. B. Senderens represented the thermal value of the reaction with solid alkali and solid sulphur by 14·4 Cals., and in dil. soln., zero. The reaction was also studied by H. Howard, F. A. Walchner, A. Lenz, H. Fleck, E. Pollacci, C. F. Capaun, T. Brugnatelli and P. Pelloggio, and E. Divers and T. Shimidzu. The thiosulphate is also produced by the action of sulphur on alkali or alkaline earth sulphates, phosphates, or chromates. Thus, T. Salzer gave $nNa_4P_2O_7+12S+3H_2O=2Na_2S_5+Na_2S_2O_3+6Na_3HP_2O_7+(n-6)Na_4P_2O_7$. The reactions were studied by W. Selezneff, J. B. Senderens, E. Filhol and J. B. Senderens, and A. Girard.

Thiosulphates are produced by the action of hydrogen sulphide or alkali sulphides on sulphur dioxide or sulphites. Thus, L. N. Vauquelin: $2Na_2S+3SO_2=2Na_2S_2O_3+S$; and E. Drechsel, $Na_2S_2O_7+2NaSH=Na_2SO_4+Na_2S_2O_3+H_2S$; the Chemische Fabrik Griesheim-Elektron, $2NaHSO_3+2Na_2S+2SO_2=3Na_2S_2O_3+H_2O$; F. Raschig represented the reaction: $6NaHSO_3+2Na_2S=2Na_2SO_3+3Na_2S_2O_3+3H_2O$. The reaction between hydrogen sulphide and sulphurous acid is discussed in connection with the former, and also in connection with the polythionates. F. Förster and co-workers showed that it can be represented by the balanced reaction: $H_2S+H_2SO_3\rightleftharpoons H_2S_2O_2+H_2O$, where the intermediate product is converted by an excess of sulphurous acid into sulphoxylic acid, which becomes polymerized to thiosulphuric acid: $H_2S_2O_2+H_2SO_3+H_2O\rightarrow 3H_2SO_2$ and $2H_2SO_2\rightarrow H_2S_2O_3+H_2O$. The production of thiosulphuric acid may, therefore, be expected to be the end-point of the changes if the reaction can be conducted under conditions such that the $H^{\bullet}$-ion concentration is insufficient to affect the stability of the thiosulphate anion. These conditions are realized experimentally when aq. soln. of sodium hydrosulphide and sodium hydrosulphite in the mol. proportion 1 : 2 are mixed, whereby sodium thiosulphate is obtained readily and in a high degree of purity: $2NaHS+4NaHSO_3=3Na_2S_2O_3+3H_2O$. The preparation of sodium thiosulphate from sodium sulphide and sulphur dioxide or from sodium sulphite and hydrogen sulphide occurs very smoothly and almost without separation of sulphur when alkali hydroxide is added initially to the soln. in such amount as to lead ultimately to the presence of sodium hydrogen sulphide and sodium hydrosulphite in the correct proportions. H. Bassett and R. G. Durrant added that the synthesis of the thiosulphate here involves the consecutive reactions $H_2S+H_2S_2O_5\rightleftharpoons HO.S.O.S.OH+S(OH)_2$; $H_2S+(HO)_2S\rightleftharpoons 2S+2H_2O$; and

$S+H_2SO_3 \rightleftharpoons H_2S_2O_3$. Alkali favours the thiosulphate formation in the last reaction. Hence, in alkaline soln. both thiosulphate and a mixture of sulphide and sulphite are equally stable. Only in the neighbourhood of the neutral point is a synthesis of thiosulphate by this method possible. Sulphide and sulphite do not react in alkaline soln. The reactions were also studied by E. F. Anthon, H. V. Tartar and C. Z. Draves, E. Mitscherlich, E. Divers and T. Shimidzu, and the Grasselli Chemical Co. L. A. Buchner also showed that hydrogen sulphide or an alkali sulphide may furnish a thiosulphate by reacting with boiling soln. of different alkali salts in air—*e.g.* borates, chlorates, acetates, tartrates, and phosphates; and G. Chancel and E. Diacon, with tetrathionates: $Na_2S+Na_2S_4O_6=S+2Na_2S_2O_3$.

Thiosulphates are also formed by the oxidation of soln. of sulphides or polysulphides. Thus, in the electrolysis of soln. of sodium sulphide or hydrosulphide, F. W. Durkee observed that the thiosulphate is formed as an intermediate product of the oxidation of sulphides to sulphates. During the electroylsis of a dil. soln. of sodium sulphide (containing about 3·4 grms. of sodium in 400 c.c.) by a current of about 3 amps., hydrogen was evolved at the cathode, and the liquid became yellow, at first around the cathode and ultimately throughout; light yellow sulphur then appeared on the anode, but scaled off again, and in greater part dissolved; fine white sulphur next separated near the surface of the liquid about the anode, but dissolved as it sank through the soln. until a certain stage of the electrolysis, when the yellow colour of the liquid disappeared and the white sulphur settled in the beaker; subsequently more oxygen escaped than at any previous stage. The separation of white sulphur is characteristic of the oxidation of thiosulphate, whilst the separation of yellow sulphur is incidental to the presence of polysulphide. These facts indicate that the course of oxidation of sodium sulphide by electrolysis is similar to that of its oxidation by air; the sulphide is first oxidized to hydroxide and thiosulphate, the latter passing to sulphate with separation of sulphur; this sulphur dissolves in unaltered sulphide to form polysulphides, which are oxidized to thiosulphate with separation of sulphur. Thus during the electrolysis, sulphides disappear first, then the hydroxide, and finally the thiosulphate, the sulphate being virtually the end product. On electrolyzing sodium sulphide soln. with an alternating current, the platinum electrodes dissolved, whereas no such dissolution was noticed in the case of the direct current electrolysis. A. Scheurer-Kestner holds that the sodium sulphide is oxidized directly to sulphate without the intermediate formation of thiosulphate. G. Lunge and co-workers have studied the oxidation of sodium sulphide in air. There are two stages in the process. In dil. soln., the oxidation, even in boiling liquor, does not proceed beyond the thiosulphate: $2Na_2S+2O_2+H_2O=Na_2S_2O_3+2NaOH$. As the liquor becomes concentrated, the thiosulphate is reduced to sulphide and sulphite, and no sulphate is formed: $3Na_2S_2O_3+6NaOH=2Na_2S+4Na_2SO_3+3H_2O$. This is confirmed by the work of H. Schäppi. If the alkali sulphide be fused, air may oxidize the sulphide to sulphite and finally to sulphate. If alkali nitrate be present, there is no oxidation below 138°; above 138°, oxidation sets in, $Na_2S+3NaNO_3=3NaNO_2+Na_2SO_3$; E. W. Parnell said that no trace of ammonia is formed, even at 288°, but G. Lunge and co-workers showed that when the temp. has risen above 170°, ammonia is produced in large quantities. From 155° to 180° the oxidation of the sulphide is more energetic and sodium sulphate is formed by the oxidation of the sulphite: $Na_2SO_3+NaNO_3=NaNO_2+Na_2SO_4$; and from 180° to 192°, the reactions are: $Na_2SO_3+NaNO_3=Na_2SO_4+NaNO_2$; $Na_2S+4NaNO_3=Na_2SO_4+4NaNO_2$; and $Na_2S+NaNO_3+2H_2O=Na_2SO_4+NH_3+NaOH$. If iron be present, the oxidation sets in below 138°, and sulphate is formed as well as ammonia and nitrogen, and no appreciable quantity of thiosulphate is formed during the whole action between 138° and 163·5. The reaction was also studied by P. Pauli, and G. E. Davis. E. E. Naef found that the oxidation of powdered hydrated sodium sulphide proceeds at ordinary temp. in the presence of finely divided active charcoal. H. Molitor discussed the manufacture of sodium thiosulphate by oxidizing calcium sulphide in air, and then treating the product with sodium sulphate by the process devised by H. Buff. F. Hefti and W. Schilt obtained thiosulphates by oxidizing hydrogen sulphide with nitrites. H. C. Jones also showed that alkali polysulphides form thiosulphates by atm. oxidation: $2Na_2S_5+3O_2=2Na_2S_2O_3+6S$. P. Kircheisen obtained a soln. of sodium hydrosulphide by treating a soln. of barium sulphide with sodium hydrosulphate or hydrocarbonate, or with equimolar proportions of the free acids and the normal salts, and allowed the soln. to oxidize.

M. Schaffner, J. Townsend and J. Walker, E. Kopp, W. S. Losh, etc., prepared the thiosulphate from the calcium thiosulphate, obtained in the regeneration of soda from the black-ash process, by double decomposition with sodium sulphate, and crystallizing out the sodium thiosulphate. The manufacture from the waste of the Leblanc soda process cannot continue because the exhaustion of the available waste is only a question of time now that process has been superseded by electrolytic methods.

P. de Clermont and J. Frommel, P. Kirchesen, V. Legrip, A. Colson, and E. Drechsel obtained the thiosulphate by boiling the aq. soln.: $Na_2S_5+3H_2O=Na_2S_2O_3+3H_2S$; H. Brunner, by treatment with sodium nitrate; W. Spring, by oxidation with iodine: $Na_2S+Na_2SO_3+I_2=Na_2S_2O_3+2NaI$; K. W. Jürisch, P. Pauli, and E. Carey and co-workers, R. Powell and W. Atkins, and E. Donath and F. Müllner, by oxidation with manganese dioxide: $2Na_2S+8MnO_2+H_2O=Na_2S_2O_3+2NaOH+4Mn_2O_3$; or with dichromates: $2Na_2S_5+4Na_2Cr_2O_7+H_2O=5Na_2S_2O_3+2NaOH+4Cr_2O_3$.

Thiosulphates are produced by the union of sulphur with sulphites. Thus, by boiling an aq. soln. of a sulphite with sulphur: $Na_2SO_3+S=Na_2S_2O_3$, H. Bassett and R. G. Durrant showed that the reaction is reversible, but the thiosulphate is very stable in alkaline soln., so that thiosulphate is readily formed by boiling alkaline sulphite soln. with sulphur. Nevertheless, even in the alkaline soln. there may be a perfectly definite although very small dissociation into sulphite and sulphur. If alkaline thiosulphate soln. containing alkali sulphide are boiled in absence of air, they become deep yellow owing to formation of polysulphide, the extra sulphur for which is obtained from the thiosulphate. A similar result is obtained by boiling an alkaline thiosulphate soln. with sodium formaldehydesulphoxylate. The yellow soln. obtained gives an immediate precipitate of lead sulphide with lead plumbite, showing that sulphide is formed on alkaline hydrolysis of sulphoxylate. The equilibrium between sulphide and thiosulphate may be written $Na_2S+Na_2S_2O_3 \rightleftharpoons Na_2S_2+Na_2SO_3$, although higher polysulphides might result as well. Such a reaction does not necessarily involve any dissociation of thiosulphates into sulphite and sulphur. There can be little doubt that it is because of such equilibria that a trace of hydrogen sulphide greatly accelerates the reaction between sodium sulphite and sulphur. Sometimes there is a long delay before sulphur begins to dissolve in boiling sodium sulphite soln., and in such cases the effect of passing a few bubbles of hydrogen sulphide into the soln. is very marked; once the action has commenced it proceeds smoothly. The catalytic action of sulphide has been referred to by H. E. Watson and M. Rajagopalan, and L. Hargreaves and A. C. Dunningham. Alkali also catalyzes the reaction owing to the production of sulphide by hydrolysis of the sulphur. It must be supposed that sodium sulphide or hydrogen sulphide is more efficient in detaching atoms of sulphur from solid sulphur than is sodium sulphite. The manufacturing process based on this reaction has been described by L. Hargreaves and A. C. Dunningham. They represented the rate of the reaction with sulphur, sulphite, and water eq. to 55·6 per cent. $Na_2S_2O_3$, agitated at 80°, by the curves,

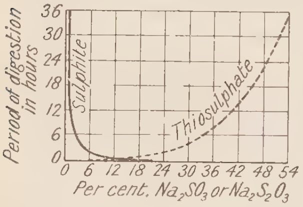


FIG. 108.—Progress of the Conversion of Sulphite to Thiosulphate.

Fig. 108. These curves show that a sat. soln. of sulphite is first formed, and that its conversion into thiosulphate proceeds rapidly. The presence of thiosulphate in the soln. decreases the solubility of the sulphite, so that as the conc. of the thiosulphate increases that of the sulphite decreases; and with the decrease in the conc. of sulphite there is a corresponding decrease in the rate of formation of the thiosulphate. The reaction was also studied by H. E. Watson and M. Rajagopalan, who said that the velocity of the reaction between sodium sulphite and sulphur depends almost entirely on the rate of dissolution of the sulphur, and is not governed by the conc. of the sulphite soln. Dilution, however, caused a slight increase in the percentage conversion. Sodium sulphide exerts a catalytic influence; and freshly prepared sulphur dissolves more quickly than aged sulphur. F. Rüsberg treated soln. of sulphide with a gas containing sulphur dioxide. E. Sidler heated a dry mixture of sulphur with a sulphite or with a hydrosulphite and hydrocarbonate at 120°–130°; V. Faget showed that if the normal sulphite be replaced by a hydrosulphite, a sulphate and only traces of thiosulphate are formed.

The Verein chemischer Fabriken prepared it by the action of sulphur dioxide on a mixture of alkali hydrocarbonate and sulphur. G. Halphen produced thiosulphate by electrolyzing an alkali sulphite; M. G. Levi and M. Voghera worked at 25° with a conc. soln. of sodium sulphide in the cathode compartment, and a feebly alkaline but conc. soln. of sodium sulphite in the anode compartment; H. von Pechmann and P. Manck, by boiling a sulphite with formic acid; E. Mitcherlich, P. Schützenberger, and H. A. Bernthsen, by dissolving zinc, iron, etc., in sulphurous acid; and B. Rathke, by the action of selenium on alkali sulphites. Thiosulphates are also formed by the decomposition of an aq. soln. of amidosulphites, hyposulphites, trithionates, tetrathionates, and pentathionates—*q.v.* M. J. Fordos and A. Gélis, and O. Ruff and E. Geisel also observed that thiosulphates are produced by the hydrolysis of nitrogen tetrasulphide: $2N_4S_4+15H_2O=(NH_4)_2S_2O_3+2(NH_4)_2S_3O_6+2NH_3$, or, in the presence of alkali: $6NaOH+N_4S_4+3H_2O=Na_2S_2O_3+2Na_2SO_3+4HN_3$. The subject was reviewed by R. Hazard.

Sodium thiosulphate as it crystallizes from aq. soln., at ordinary temp., is in the form of the *pentahydrate*, $Na_2S_2O_3.5H_2O$. According to P. Jochum,[3] if the supersaturated soln. be treated with alcohol, an oily liquid is obtained which, when treated with 98 per cent. alcohol, furnishes the *trihydrate*, $Na_2S_2O_3.3H_2O$; and, according to W. W. J. Nicol, supersaturated soln. of thiosulphate deposit the *dihydrate*, $Na_2S_2O_3.2H_2O$; he also gave less definite evidence of a possible *hemitrihydrate*, $Na_2S_2O_3.1\frac{1}{2}H_2O$. L. K. Riggs obtained anhydrous thiosulphates by heating the hydrated salt in an atm. of water-vapour to a temp. high enough to drive off the water of crystallization, and holding the product at that temp. until it is removed from the water-vapour so as to prevent recombination.

From F. Guthrie's observations on the eutectic mixtures, and S. W. Young and co-workers' on the transition points, W. W. Taylor's on the solubility, *S*, per cent. $Na_2S_2O_3$, the stable solid phases, and the solubilities appear to be:

	−3·9°	−11°	0°	10°	20°	40°	50°	60°	80·5°	100°
S .	15·04	30·03	34·43	37·90	41·17	50·65	62·92	67·39	71·33	72·68
Solid phases	Ice		$Na_2S_2O_3.5H_2O$				$Na_2S_2O_3.2H_2O$		$Na_2S_2O_3$	

The results for the stable hydrates are illustrated by Fig. 109. The liquid is very prone to form metastable and supersaturated soln. The dotted lines represent metastable hydrates which are illustrated in more detail in Figs. 102 to 104. The transition temp. for $Na_2S_2O_3.5H_2O \leftrightharpoons Na_2S_2O_3.2H_2O+3H_2O$, given by T. W. Richards and J. B. Churchill, is 47·9°; S. W. Young and W. E. Burke, 48·2°; and by A. von Trentinaglia, 48·09°. H. M. Dawson and C. G. Jackson found that the transition temp. was lowered 0·554° if 0·4425 grm. of urea be associated with 65·4 grms. of thiosulphate; 0·857° with 0·6940 grm. of urea per 65·6 grms. of thiosulphate and 1·095° with 1·2605 grms. urea per 90·06 grms. of thiosulphate. The transition point for the passage of the dihydrate to the anhydrous salt given by S. W. Young and W. E. Burke is 68·5°. Observations on the solubility were also made by F. Rudorff, G. J. Mulder, P. Kremers, L. Wöhler and J. Dierksen, and H. Schiff. The α-**pentahydrate** is the ordinary commercial salt. S. W. Young and W. E. Burke said that the pentahydrate is stable at all temp. below 48·2°. If any of the other forms of thiosulphate, contained in tubes, are cooled to about —35° and then allowed to warm up, the α-pentahydrate grows through the mass of crystals and soln. contained in the tubes. The crystals start to grow at the lower temp. but grow very slowly; the rate of growth increases rapidly with the temp., and soon becomes very great. F. Parmentier and L. Amat reported a labile or unstable modification of the pentahydrate which furnishes long fine needles. On standing, the opaque mass of fine crystals gradually becomes clearer, in some cases perfectly transparent, to the eye, resembling a very clear jelly. Its other properties remain unchanged. If partially melted and allowed to solidify, it comes down in fine needles, as at first. It is called the β-**pentahydrate**. It was obtained by S. W. Young and J. P. Mitchell by heating the ordinary or α-form at 80°–100° for a few minutes in a sealed glass tube, and cooling to —10° or —20°, when the product solidifies in long needles. The *γ-pentahydrate* of S. W. Young and J. P. Mitchell was shown by S. W. Young and W. E. Burke to be really a **hexahydrate**, and it was made as in the case of the β-pentahydrate, but with a little water in the tube. The **tetrahydrate** is produced when the β-pentahydrate is heated above 30°. The crystals closely resemble those of the β-pentahydrate. The α-**dihydrate** is the ordinary form of the dihydrate which was obtained by W. W. Taylor, etc., by heating the pentahydrate above its transition temp., and allowing it to cool, at, say, 50° to 55°, until crystallization starts. It forms coarse needles resembling the α-pentahydrate. The β-**dihydrate** is obtained by keeping the tritatetrahydrate at a temp. slightly above 0° when it forms thin, radiating plates. The **hemitrihydrate** or sesquihydrate is formed by keeping the hexahydrate at about 14·2° for some time, when the containing tubes furnish very fine, needle-like crystals resembling those of the tritatetrahydrate, and they grow more rapidly. The **tritatetrahydrate** was obtained by keeping the hexahydrate at about 15° in a superfused state. The crystals appear as fine needles, and if the soln. is at all conc. it becomes filled with them, and appears to be almost completely solidified, when in reality the crystals form but a small proportion of the total mass. The α-**monohydrate** is formed when the α-pentahydrate is melted and kept in a surfused state at ordinary temp. for a day or two; and it forms in soln. of the anhydride at temp. below 50°; and in soln. of the tetrahydrate at temp. above 40°. It grows very slowly in conc. soln., forming either long, coarse needles, or small rectangular prisms according to the conditions under which the crystallization occurs. The β-**monohydrate** is obtained from the hemitrihydrate by transition below 50°. The crystals resemble those of the α-monohydrate. The γ-**monohydrate** is produced when β-dihydrate is heated above 35°; the crystals resemble those of the other monohydrates. The **hemihydrate** is formed by heating the γ-monohydrate at temp. above 50°; the crystals resemble those of the monohydrate. The anhydrous salt is formed in rectangular prisms when any of the other hydrates are heated at temp. above 70°.

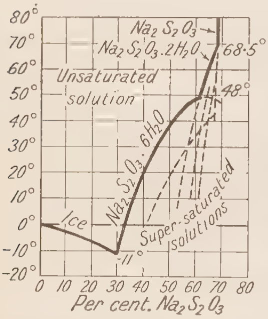
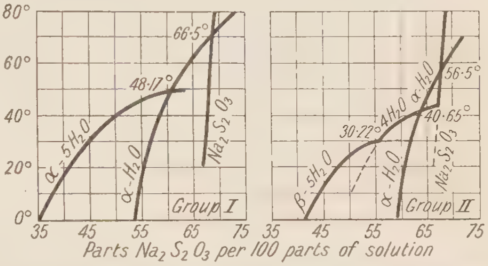


FIG. 109.—The Solubility of the Stable Hydrates of Sodium Thiosulphate.

M. Picon studied the heating curves of sodium thiosulphate and water obtained by spontaneous crystallization in nuclei-free, closed vessels, and said that a *decahydrate*, $Na_2S_2O_3.10H_2O$, and a *dodecahydrate*, $Na_2S_2O_3\ 12H_2O$, exist, but the former can alone be isolated at a low temp., the latter decomposes. He concluded that hydrates do not exist in soln.; and that the tertiary, quaternary, and quinquinary hydrates of S. W. Young and W. E. Burke do not exist. All the hydrates are either primary or secondary.

Thus, according to S. W. Young and W. E. Burke, there are thirteen crystalline modifications of sodium thiosulphate; twelve of these are hydrated, namely, one hexahydrate, two pentahydrates, one tetrahydrate, two dihydrates, one hemitri- or sesquihydrate, one tritatetrahydrate, three monohydrates, and one hemihydrate. They separate these hydrates into five groups—primary, secondary, tertiary, quaternary, and quintary—on the basis of their conduct in undergoing transition with rising temp., and these transitions are not always in accord with rule of successive reactions—**2**. 19, 14. The primary, ordinary, or *α-pentahydrate* of group I, Fig. 110, undergoes transition at 48·17° into primary or *α-dihydrate*, but may be superheated past this transition temp. to the m.p. Sooner or later, the α-dihydrate appears in fusions kept near the m.p.; but the reverse transition occurs only with difficulty. With rising temp., the α-dihydrate passes into the anhydride at 66·5°. Expressing the solubilities in grams of $Na_2S_2O_3$ per 100 grms. of water, the primary α-pentahydrate furnishes, Fig. 110, and



FIGS. 110 and 111.—Solubilities of the Hydrates of Sodium Thiosulphate.

	0°	5°	10°	15°	20°	25°	35°	40°	45°
α-5H_2O .	33·40	35·33	37·37	39·11	41·20	43·15	45·19	50·83	55·33

and for the primary α-dihydrate:

	0°	5°	10°	20°	30°	40°	50°	60°	65°
α-2H_2O .	52·73	53·45	53·94	55·15	57·13	59·38	62·28	65·68	68·04

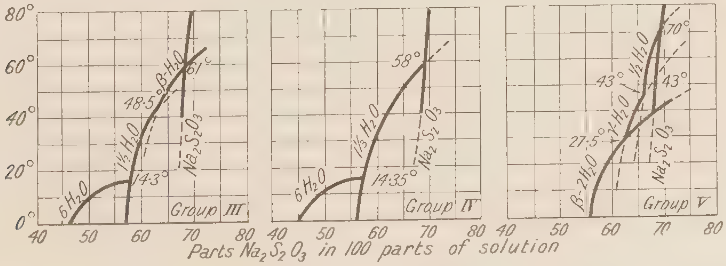
In group II, Fig. 111, the *β-pentahydrate* superheats only slightly, passing into the *tetrahydrate* at 30·22° with great facility; similarly the reverse change takes place very readily without undercooling. The change from the tetrahydrate to the *α-monohydrate* at 40·65° takes place with difficulty and superheating; and similarly, the α-monohydrate readily undercools. If undercooled at ordinary temp., the α-monohydrate passes directly into the β-pentahydrate; and at a higher temp., 56·5°, the anhydride is formed. With the same units as before, the solubility of the secondary or θ-pentahydrate is:

	0°	5°	10°	15°	20°	25°	30°
β-5H_2O .	41·96	43·56	45·25	47·27	49·38	52·15	56·57

that of the tetrahydrate is 58·59 at 33·5°, 60·51 at 36·2°, and 62·80 at 38·6°; and that of the α-monohydrate is:

	0°	10°	20°	30°	40°	50°	55°
α-H_2O .	60·47	61·04	62·11	63·56	65·22	66·82	67·90

In group III, Fig. 112, the *hexahydrate* was regarded as a *γ-pentahydrate* by S. W. Young and J. P. Mitchell, and they said that it acts as a tertiary hydrate, and



FIGS. 112, 113, and 114.—Solubilities of the Hydrates of Sodium Thiosulphate.

may be superheated even to fusion without the appearance of the hemitrihydrate. The converse undercooling is also marked. The hexahydrate passes into the *hemitrihydrate* at 14·3°; and the hemitrihydrate into the *β-monohydrate* at 48·50°—there being here no marked undercooling or superheating. At 61°, the β-monohydrate passes into the anhydride. Expressing solubilities as before, the value for the hexahydrate is 46·14 at 0°, 48·44 at 5°, 51·66 at 10°, and 54·96 at 13°; for the hemitrihydrate:

	0°	5°	10°	20°	30°	40°	45°	47·5°
$1\frac{1}{2}H_2O$.	57·42	57·84	58·28	59·28	60·78	62·60	63·97	64·68

and for the β-monohydrate, 64·78 at 47·5°, 65·30 at 50°, 65·89 at 52·5°, 66·45 at 55°, and 68·07 at 60°. The hydrates in group IV, Fig. 113, behave like those in group III; the hexahydrate—the same as the hexahydrate in group III—superheats up to its m.p., and if the fused mass is held for some time a degree or two of temp. above the m.p., the *tritatetrahydrate* appears with the transition temp. 14·35°; the tritatetrahydrate passes into the anhydride at 58°. Expressing solubilities as before:

	0°	5°	10°	20°	30°	40°	50°	55°
$1\frac{1}{3}H_2O$.	57·63	58·08	58·49	59·57	61·03	62·95	65·45	67·07

In group V, Fig. 114, the *β-dihydrate* may superheat past the mono- but also past the hemihydrate, and when the transition then occurs, the monohydrate is first formed. The *γ-monohydrate* supercools but slightly with respect to the dihydrate. The γ-monohydrate readily superheats some 10° above the transition temp. into the *hemihydrate*; the hemihydrate readily supercools with respect to the γ-monohydrate, and also with respect to the superheated β-dihydrate. The transition point for the β-dihydrate into the γ-monohydrate is 27·5°; for the γ-monohydrate into the hemihydrate, 43°; and for the hemihydrate into the anhydride, 70°. Expressing solubilities as before, for the β-dihydrate:

	0°	50°	10°	20°	30°	40°	50°	55°
$\beta\text{-}2H_2O$.	57·63	58·08	58·49	59·57	61·03	62·95	65·45	67·07

for the γ-monohydrate:

	30°	35°	40°	45°	50°	55°
$\gamma\text{-}H_2O$.	63·34	64·07	64·75	65·58	66·58	67·59

and for the hemihydrate:

	25°	35°	40°	50°	60°	70°
$\frac{1}{2}H_2O$.	64·21	64·60	64·99	66·02	67·40	69·04

The anhydrous sodium thiosulphate furnishes prismatic **crystals.** The α-pentahydrate, or the ordinary form of sodium thiosulphate, was found by F. de la Provostaye to furnish monoclinic prisms with the axial ratios $a:b:c=0·3508:1:0·2745$, and $\beta=103° 58'$. The crystals were also examined by H. de Sénarmont, and C. F. Rammelsberg. The **optic axial angle** is nearly 100°; and H. Dufet gave $2H_\alpha=83° 15'$; $2V=80° 16'$ for Na-light, and $2E=154° 7'$; while A. des Cloizeaux gave $2E=154° 1'$ for red-light; 154° 14′ for yellow-light; and 155° 57′ for blue-light. A. Fock and K. Klüss obtained similar crystals from alcoholic soln. F. Parmentier and L. Amat said that the crystals of the β-pentahydrate are probably monoclinic. The crystalline forms of the other hydrates of this salt have not been determined; many of these cannot be handled except in sealed tubes. G. T. Gerlach gave 1·667 for the **specific gravity** of the anhydrous salt at 14°/4°; and for the α-pentahydrate, H. J. Buignet gave 1·672; H. Schiff, 1·734; W. C. Smith, 1·723; J. Dewar, 1·729 at 17°, and 1·7635 at the temp. of liquid air, −188·7°; and H. Kopp, 1·736 at 10° on a sample which had been melted and crystallized many times, and he reported that on melting, the pentahydrate expands 5·1 per cent. in vol. H. Schiff found the sp. gr., D, of soln. with p per cent. of the pentahydrate, at 19°, to be:

p .	5	10	15	20	25	30	35	40	45	50
D .	1·026	1·053	1·081	1·109	1·136	1·168	1·199	1·230	1·262	1·295

Other observations on the sp. gr. of these soln. were made by P. Kremers, W. W. J. Nicol, and H. Baumhauer. F. Flöttmann observed that the sp. gr. of a one per cent. soln. at 15°, 20°, and 25° are respectively 1·0075, 1·0065, and 1·0052. D. O. Masson studied the **solution volume** and the solvation of the molecule. H. Schiff and U. Monsacchi observed that when the salt is dissolved in water, increasing contraction occurs until 40 per cent. of the salt is present; the contraction then decreases until 78 per cent. is present when the contraction is zero; thereafter, an expansion occurs. L. de Boisbaudran observed the following percentage change of vol.—referred to the vol. of the solid salt—when *p* grms. of salt are present per 100 grms. of soln.:

p . . .	1·5	7	12	35	60	85	100
Change in vol.	−17·97	−15·09	−13·35	−7·68	−2·74	+2·00	+4·54 per cent.

The subject was studied by J. N. Rakshit. W. W. J. Nicol found that for the **viscosity**, if the time of flow of water at 20° be 100, that of a 79 per cent. soln. of the thiosulphate at 20° is 834·4; at 25°, 685·2; at 30°, 574·5; at 35°, 487·1; and at 40°, 420·7. I. K. Taimni also measured the viscosity of these soln. when superheated. J. Dewar gave 0·0000969 for the coeff. of **thermal expansion** over the range 17° to the temp. of liquid air, −188·7°. Summarizing the **transition temperatures** by S. W. Young and W. E. Burke, α-pentahydrate$\rightleftharpoons$α-dihydrate, 48·17°; α-dihydrate$\rightleftharpoons$anhydride, 68·5; β-pentahydrate$\rightleftharpoons$tetrahydrate, 30·22°; β-pentahydrate$\rightleftharpoons$α-dihydrate, 30·46°; tetrahydrate$\rightleftharpoons$α-dihydrate, 31·50°; tetrahydrate $\rightleftharpoons$α-monohydrate, 40·65°; α-monohydrate$\rightleftharpoons$anhydride, 56·5°; hexahydrate $\rightleftharpoons$hemitrihydrate, 14·25°; hexahydrate$\rightleftharpoons$tritatetrahydrate, 14·3°; hemitrihydrate$\rightleftharpoons$β-monohydrate, 48·5°; β-monohydrate$\rightleftharpoons$anhydride, 61°; tritatetrahydrate$\rightleftharpoons$anhydride, 58°; β-dihydrate$\rightleftharpoons$γ-monohydrate, 27·5°; γ-monohydrate $\rightleftharpoons$hemihydrate, 43°; and hemihydrate$\rightleftharpoons$anhydride, 70°. H. Kopp gave 45° for the **melting point** of the α-pentahydrate; T. W. Richards and J. B. Churchill, and W. W. Taylor, 47·9°; P. Kremers, and H. Debray, 48°; A von Trentinaglia, 48·1°; W. A. Tilden, 48·5°; and G. J. Mulder, 50°. S. W. Young and W. E. Burke gave 48·45° for the m.p. of the α-pentahydrate; F. Parmentier and L. Amat, 32° for β-pentahydrate; S. W. Young and W. E. Burke, 41·65° for the tetrahydrate; and 14·35° for that of the hexahydrate. E. N. Gapon studied some relationships of the m.p. A. Boutaric measured the lowering of the f.p. of the pentahydrate by an addition of urea, glucose, cane-sugar, sodium chloride, chlorate, nitrate, or sulphate. The fused pentahydrate readily passes into the surfused state when cooled, and this salt has been used in numerous investigations on the phenomenon in general—*e.g.* by A. Blümcke, S. W. Young and co-workers, etc.—*vide* **1.** 9, 6. C. Pape found that the undamaged crystals effloresce at 33°; and E. A. Letts showed that when kept for two months in vacuo over sulphuric acid, the salt loses almost all its water of crystallization, and the remainder at 100°. The salt was found by C. Pape to become anhydrous at 215°, and to decompose at 220°–225° with the formation of sulphur; M. Berthelot gave 200°; and E. A. Letts, 233°, provided the salt be rapidly heated—if slowly heated, the hydrated salt can decompose at 100°. A. Jaques also observed that if the hydrated salt be quickly heated in a test-tube, it is decomposed near the hot wall of the tube while water is still being evolved, and much hydrogen sulphide is formed—presumably from the water. Hence, he added that the nascent sulphur, together with the reducing action of sodium sulphite formed in the decomposition, is sufficient to break up the water: $Na_2SO_3+S+H_2O=H_2S+Na_2SO_4$. Sulphur, sodium sulphite, and sodium sulphate are present in the residue. It is noteworthy that no sulphur dioxide is given off; so that the presence of the sodium sulphite appears to be necessary for the action to go on, as otherwise the oxygen out of the water would probably unite with the free sulphur which is present in the residue, forming sulphur dioxide. According to M. Picon, the hydrated salt loses water only on a prolonged heating in vacuo at 300°. L. N. Vauquelin, and C. F. Rammelsberg found that if the anhydrous salt be strongly heated, sulphur is formed, and the mass blackens; and, on cooling, there remains a mixture of sodium pentasulphide and sulphate. M. Picon added that the main decomposition (which proceeds very slowly at 120° and is complete in six hours at 380°–385°) is into sodium sulphite and free sulphur, small quantities of sulphate and polysulphide also being formed. Above 400°, the proportion of sulphate and polysulphide increases until rapid heating at 600° causes almost complete decomposition in accordance with the equation $4Na_2S_2O_3=3Na_2SO_4+Na_2S_5$. On account of this reaction, sodium thiosulphate was recommended by J. Landauer as a blowpipe reagent. H. Debray found that the **vapour pressure** of the pentahydrate remains unchanged while it is melting; and H. Lescoeur found the **dissociation pressure** of the pentahydrate is 4 mm. at 20°, and 8·1 mm. at 40°. The vap. press. of a sat. soln. of the salt at 20° is 12 mm., and at 40°, 33·2 mm. A. Speransky represented the vap. press. of the pentahydrate by $p=k\{(\theta-75{\cdot}454)\theta^{-1}\}50$, where $\log k=7{\cdot}3934$. A. G. Bergman's measurements of the vap. press. of the hydrated salt are summarized in Fig. 115. H. Predvoditeleff studied the rate of dehydration of the salt. G. Tammann observed the **lowering of the vapour pressure** of water was 16·0, 64·2, 191·1, and 361·0 mm. by the addition of 8·91, 32·86, 83·93, and 181·48 grms. of salt respectively per 100 grms. of water at 100°. The **boiling points** of aq. soln. with g grms. of $Na_2S_2O_3$ per 100 grms. of water, were found by G. T. Gerlach to be:

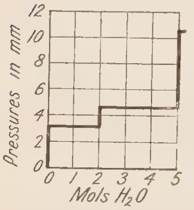


FIG. 115.—Vapour Pressure of Hydrated Sodium Thiosulphate.

g	0	14	27	59	104	152	201	262	348
B.p.	100°	101°	102°	105°	110°	115°	119°	123°	126°

F. M. Raoult gave 39·9 for the mol. **lowering of the freezing point** in water, and T. W. Richards and H. B. Faber for 3·198, 6·396, and 8·470 grms. of salt per 100 grms. of water respectively obtained a lowering of 0·855°, 1·594°, and 1·980° respectively. F. J. Faktor obtained mol. wt. 59·92–60·5 from the depression of the f.p. of soln.; and from the **raising of the boiling point,** 77·9 to 79·2. Hence, at low temp., the salt forms the ions $2Na^{\cdot}$, and S_2O_3'', but at higher temp. it forms the ions $Na^{\cdot}$ and NaS_2O_3'. L. Bruner found the **specific heat** of the surfused salt to be:

	94°–17°	83°–16°	65°–16°	55°–16°	47°–17°	36°–17°	13°–2°
Sp. ht.	0·584	0·587	0·590	0·599	0·602	(0·595)	0·563

There are thus indications of a maximum at about 48°; the bracketed number is probably misprinted as 0·395 in the original. A. von Trentinaglia gave 0·447 for the sp. ht. of the solid pentahydrate between 11° and 44°; and 0·569 for the molten salt between 13° and 98°. The **heat of fusion** is 37·6 Cals. at 9·86°. M. Berthelot gave for the **heat of formation** of the salt from its elements 262·600 Cals.; and in soln., 264·0 Cals. J. Thomsen gave $(Na_2,S_2,O_3,5H_2O)=193{\cdot}99$ Cals.; and E. Filhol and J. B. Senderens gave $(S_2O_3,2Na)=25{\cdot}10$ Cals.; $(Na_2O_{\text{soln.}},S_2O_2)=27{\cdot}0$ Cals.; F. Rüdorff found that when 110 parts of salt are mixed with 100 parts of water at 10·7°, the temp. is lowered 18·7° to −8°. M. Berthelot gave −10·82 Cals. for the **heat of solution,** and J. Thomsen, −11·73. M. Berthelot found −5·8 Cals. for the heat of soln. of the α-pentahydrate, and J. Thomsen, −5·7 Cals.; and F. Parmentier and L. Amat gave −4·4 Cals. for the β-pentahydrate. The **indices of refraction** found by H. Dufet were for Li-light, $\alpha=1{\cdot}4849$, $\beta=1{\cdot}5038$, and $\gamma=1{\cdot}5311$; for Na-light, $\alpha=1{\cdot}4886$, $\beta=1{\cdot}5079$, and $\gamma=1{\cdot}5360$; and for Tl-light, $\alpha=1{\cdot}4919$, $\beta=1{\cdot}5117$; and $\gamma=1{\cdot}5405$. B. C. Damien also measured the index of refraction of this salt. F. Flöttmann found the indices of refraction of one per cent. soln. at 15°, 20°, and 25° are respectively 1·33551, 1·33513, and 1·33458 for the D-line. The **double refraction** is positive. J. E. Almy observed no double refraction when a soln. of sodium thiosulphate is strained by a rotating cylinder. H. Dufet measured the **dispersion** for light of different wave-lengths; while H. de

Sénarmont studied what he called the *dispersion croisée* of the crystals. V. J. Sihvonen found maxima in the **reflection ultra-red spectrum** of sodium thiosulphate at 9·1μ, 10·2μ, 15·1μ, 18·5μ, and 19·7μ. O. Stelling studied the absorption spectrum of X-rays. R. Robl observed no fluorescence with the salt in ultra-violet light. P. Bary found that the curves representing the variation of the refractive index with the conc. of the soln. is not continuous, but is made up of several right lines with different inclinations to the axis of the ordinates. Each break indicates a sudden change in the mol. conditions of the medium, and most probably corresponds to the formation of a new hydrate in the soln. The breaks occur with soln. of the molar composition: $Na_2S_2O_3.40H_2O$, when the refractive index is 1·3658, and $Na_2S_2O_3.20H_2O$, 1·3097. C. Chéneveau also measured the indices of refraction of soln. of this salt. J. A. Fleming and J. Dewar found that water with sodium thiosulphate in soln. has at −185° a **dielectric constant** of 30 to 70—with water alone it is 2·5. F. W. Küster and A. Thiel measured the **electrical conductivity** of the molten pentahydrate; the conductivity decreases as the proportion of water decreases; and the variations of the resistance, R ohms, with the hydration expressed in terms of n mols of H_2O per mol of $Na_2S_2O_3$ in the fused salt, are:

n	6·65	6·25	5·79	5·41	4·93	4·69
R	1074·8	1133·7	1204·9	1320·2	1493·6	1575·1

A. F. Hollemann found the mol. conductivity, λ, of sodium thiosulphate to be for an eq. of the salt in v litres, at 25°:

v	32	64	128	256	512	1024
λ	101·1	107·6	113·0	117·4	120·0	120·2

at infinite dilution, $\lambda_\infty=128$, and the velocity of the $\frac{1}{2}S_2O_3$-ion is 78·8. C. Watkins and H. C. Jones found for the molar conductivity, μ mho, and percentage degree of ionization, α, for a mol of the salt in v litres:

v		4	8	16	32	128	512	1024	2048	4096
μ	0°	77·9	82·52	94·10	103·0	113·1	126·0	124·8	128·1	131·4
	15°	115·3	129·8	143·4	153·2	172·4	189·0	191·9	194·1	195·0
	25°	143·3	160·8	178·4	193·0	214·9	234·9	239·1	241·1	244·0
	35°	172·6	196·0	214·8	235·0	259·9	283·8	284·1	284·3	290·5
α	0°	52·9	62·8	71·6	78·4	86·0	95·8	94·9	97·5	100·0
	35	59·4	67·4	73·9	80·8	89·4	97·6	97·7	97·8	100·0

F. J. Faktor inferred from the electrical conductivity of aq. soln. that ionization takes place in the stages $Na_2S_2O_3 \rightleftharpoons Na^{\cdot}+NaS_2O_3'$; and $Na_2S_2O_3 \rightleftharpoons 2Na^{\cdot}+S_2O_3''$. When the soln. of sodium thiosulphate is electrolyzed, it forms sulphur, hydrogen sulphide, tetrathionic acid, sulphur dioxide, and sulphuric acid. F. W. Durkee found that the thiosulphate is an intermediate stage in the electro-oxidation of hydrosulphide soln. to sulphates; while A. Scheurer-Kestner believed that the oxidation proceeds directly to sulphate—*vide supra*. L. N. Vauquelin reported that the salt is inodorous; and has at first a cooling taste which afterwards appears bitter, slightly alkaline, and sulphurous. F. de la Provostaye, H. de Sénarmont, and L. N. Vauquelin said that the salt is deliquescent in moist **air.** F. Chaussier found that the salt is permanent in dry air, but when heated in air, it burns with a blue flame. J. Obermiller measured the hygroscopicity of sodium thiosulphate. The solubility in **water** has already been discussed—Figs. 110 to 114. C. F. Capaun showed that when heated with water, in closed vessels, it deposits sulphur until nothing is left in soln. but sodium sulphite; and if exposed to air, it deposits sulphur, and forms sodium sulphate.

According to E. V. Espenhahn, the reaction between a thiosulphate and sulphur dioxide is expressed by the equation: $2(NH_4)_2S_2O_3+3SO_2=(NH_4)_2S_3O_6+(NH_4)_2S_4O_6$. Under certain conditions, other reactions occur according to the equations (i) $2(NH_4)_2S_2O_3+3SO_2+S=2(NH_4)_2S_4O_6$, and (ii) $2(NH_4)_2S_3O_6=(NH_4)_2S_3O_6+(NH_4)_2S_5O_6$; these, however, do not influence the main reaction. L. Hargreaves and A. C. Dunningham's relations between the mutual solubilities of sodium sulphite and thiosulphite, at 80°, are shown in Fig. 116. H. P. Cady and R. Taft observed that sodium thiosulphate is appreciably soluble in liquid sulphur dioxide. L. Wöhler and J. Dierksen studied the solubility of binary and ternary mixtures of $Na_2S_2O_3$–Na_2SO_4–Na_2SO_3. The effect of sodium thiosulphate on solubilities of sodium sulphate and sulphite are :

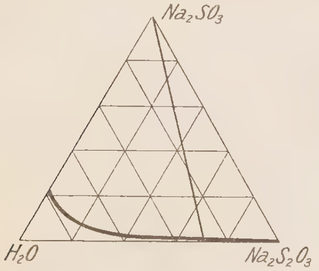


FIG. 116.—The Ternary System : $Na_2S_2O_3$–Na_2SO_3–H_2O, at 80°.

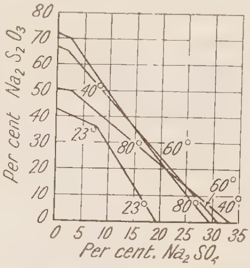


FIG. 117.—Mutual Solubilities of Sodium Sulphate and Thiosulphate.

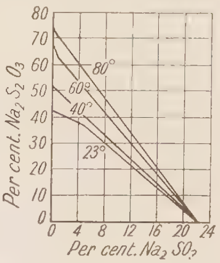


FIG. 118.—Mutual Solubility of Sodium Sulphite and Thiosulphate.

	$Na_2S_2O_3$–Na_2SO_4				$Na_2S_2O_3$–Na_2SO_3			
	23°	40°	60°	80°	23°	40°	60°	80°
$Na_2S_2O_3$	36·40	49·4	65·9	70·2	36·9	49·4	64·4	69·7
Na_2SO_4 .	7·22	1·86	1·57	1·12	—	—	—	—
Na_2SO_3 .	—	—	—	—	5·6	1·1	0·3	0·36

The corresponding curves, Figs. 117 and 118, show that the solubility of sodium thiosulphate increases rapidly with temp. and is depressed a little by the sulphate but less so by the sulphite. The mutual solubilities of the three salts are as follows when the solubilities of the individual salts are indicated in brackets :

	23°	40°	60°	80°
$Na_2S_2O_3$.	33·80(42·4)	49·30(50·7)	63·10(65·5)	69·09(71·6)
Na_2SO_4 . .	6·62(19·4)	1·75(32·5)	1·59(31·25)	1·35(30·3)
Na_2SO_3 . .	5·35(22·0)	0·63(22·0)	0·14(22·0)	0·18(22·0)

The results are plotted in Fig. 119 at 23°. R. R. Garran examined the ternary system $Na_2S_2O_3$–$4Na_2SO_4$–H_2O at 0·8, 18°, 25°, and 40°. The results at 18° and 25° are illustrated in Figs. 120 and 121. The curve *ab* denotes soln. in equilibrium with solids along the line *a′b′* which is so short that it gives only slight evidence of the formation of mixed crystals $Na_2S_2O_3.5H_2O$ and probably $Na_2SO_4.5H_2O$. The curve *bc*, Fig. 120, denotes soln. in equilibrium with solids along *b″c′*, and there is here definite evidence of the formation of mixed crystals of the two decahydrates. The two-phase dry solids along the line from *b′* to *b″* are in equilibrium with the soln. at the triple point *b*. The three curves *ad*, *de*, and *ef*, Fig. 121, represent three phases ; *ad* denotes soln. in equilibrium with mixed crystals along *a′d′*—mainly $Na_2S_2O_3.5H_2O$; *de* denotes those in equilibrium with the mixed crystals *d″e″*—mainly anhydrous Na_2SO_4 ; and *ef*, those in equilibrium with *e′f*—mainly $Na_2SO_4.10H_2O$. F. Chaussier observed that the aq. soln. has not an alkaline reaction—*vide supra*, thiosulphuric acid. C. F. Capaun, L. Bruner, and F. Parmentier measured the solubility of the pentahydrate in **alcohol ;** E. Bödtker obtained for 100 parts of absolute alcohol, 2·5 mgrms. of the anhydrous

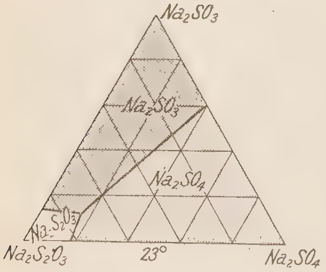


FIG. 119.—The Ternary System : Na_2SO_3–Na_2SO_4–$Na_2S_2O_3$ in Aqueous Solution at 23°.

salt, and 3·4 mgrms. of the pentahydrate—all at room temp.—100 grms. of alcohol of sp. gr. 0·941 dissolves 33·3 grms. of the salt at 15·5°. L. Bruner found that the solubility of the surfused thiosulphate in alcohol is greater than that of the ordinary solid; and F. Parmentier found that with absolute alcohol, the pentahydrate cannot be completely fused in sealed tubes, even at 100°; with alcohol of 80° (hydrometer), it melts at 41° and not at 47·9°; and with alcohol of 63°, at 33°. The salt, superfused in presence of alcohol of 80°, solidifies in the allotropic modification when cooled with a mixture of ice and salt, but the product melts at 28° instead of 32°. They found that, although the solubility of the pentahydrate is constant with the quantity of solvent (alcohol and water), the solubility of the superfused pentahydrate increases with the vol. of the solvent. The conc. of the alcohol above the superfused salt also varies, and a complex condition of equilibrium is set up between the alcohol, the water, and the anhydrous salt. J. L. Casaseca found the pentahydrate to be insoluble in **ethyl acetate**; and T. A. Edison, soluble in **turpentine.** H. Bunte represented the reaction with **ethyl bromide**: $NaO.SO_2.SNa+C_2H_5Br = NaO.SO_2.SC_2H_5+NaBr$; and $NaO.SO_2.SC_2H_5+H_2O=NaHSO_4+C_2H_5.SH$. F. C. Calvert found that the presence of $\frac{1}{1000}$th part of sodium thiosulphate in albumen did not prevent the growth of protoplasmic life and fungi. A. Berthoud and W. Berger discussed the induction of the reaction between potassium nitrite and iodine by sodium thiosulphate. A. N. Kappanna studied the reaction with **sodium bromoacetate.** V. P. Radishcheff studied the ternary system $Na_2S_2O_3$–$NaCl$–H_2O at 25°.

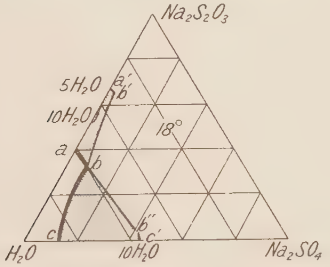


Fig. 120.—Equilibrium in the Ternary System: $Na_2S_2O_3$–Na_2SO_4–H_2O.

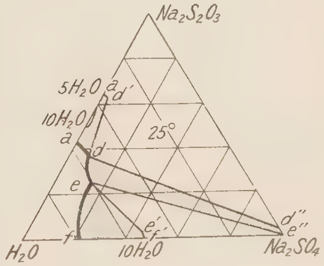


Fig. 121.—Equilibrium in the Ternary System: $Na_2S_2O_3$–Na_2SO_4–H_2O.

Many of the general methods of preparation of sodium thiosulphate refer also to **potassium thiosulphate,** $K_2S_2O_3$. E. Drechsel obtained the anhydrous thiosulphate by the action of potassium hydrosulphide on the pyrosulphate in alcoholic soln.: $KSH+K_2S_2O_7=KHSO_4+K_2S_2O_3$. J. J. Berzelius exposed alcoholic soln. of potassium di- or a higher sulphide to air in a loosely stoppered bottle and washed with alcohol the crystals which are slowly deposited. E. Sidler heated to 120°–130° a dry mixture of potassium sulphite, and sulphur, or a mixture of potassium hydrocarbonate and hydrosulphite, and sulphur. F. Kessler, and O. Döpping treated a hot soln. of potassium pentasulphide with a hot soln. of potassium dichromate added in small proportions at a time to allow the precipitate to acquire the characteristic green colour of chromic oxide: $2K_2S_5+4K_2Cr_2O_7+H_2O =4Cr_2O_3+5K_2S_2O_3+2KOH$. G. S. Kirchhoff boiled with water a mixture of sulphur with three times its weight of potassium carbonate, and eight of lime, renewing the water as it evaporated. The filtered soln. was neutralized with sulphuric acid and evaporated for crystallization—the sulphate crystallized out first, then the thiosulphate. F. Kessler used a similar process. F. Kessler, C. F. Rammelsberg, A. Fock and K. Klüss, and G. Wyrouboff obtained crystals of a *tritahydrate*, $K_2S_2O_3.\frac{1}{3}H_2O$—C. F. Rammelsberg dried his salt for 24 hrs. in vacuo; O. Döpping, of a *monohydrate*, $K_2S_2O_3.H_2O$—dried over conc. sulphuric acid—F. Kessler could not confirm this; F. Kessler, of a *tritapentahydrate*, $K_2S_2O_3.1\frac{2}{3}H_2O$; O. Döpping, of a *hemitrihydrate*, $K_2S_2O_3.1\frac{1}{2}H_2O$; and E. Mathieu Plessy, of a *dihydrate*, $K_2S_2O_3.2H_2O$. F. Kessler observed that the salt is freely soluble in water with the absorption of much heat. According to I. Jo, the solubility of potassium thiosulphate, expressed as S grms. of $K_2S_2O_3$ per 100 parts of water, is as follows :

	0°	17°	35°	60°	56·1°	65°	70°	78·3°	85°	90°
S .	96·1	150·5	202·4°	238·3°	234·5°	245·8	255·2	292·0	298·5	312·0
	$3K_2S_2O_3.5H_2O$			$K_2S_2O_3.H_2O$		$3K_2S_2O_3.H_2O$			$K_2S_2O_3$	

The results are plotted in Fig. 122. They show that the tritapenta-, mono-, di- and trita-hydrates are capable of existence. The **transition temperature** for $K_2S_2O_3.2H_2O \rightleftharpoons K_2S_2O_3.1\frac{2}{3}H_2O$ is below 17° ; that for $K_2S_2O_3.1\frac{2}{3}H_2O \rightleftharpoons K_2S_2O_3.H_2O$ is 35° ; that for $K_2S_2O_3.H_2O \rightleftharpoons K_2S_2O_3.\frac{1}{3}H_2O$ is 56·1° ; and that for $K_2S_2O_3.\frac{1}{3}H_2O \rightleftharpoons K_2S_2O_3$ is at 78·3°, so that the salt is anhydrous above 78·3°.

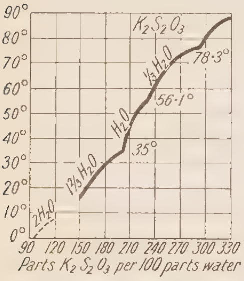


FIG. 122.—The Solubility of Potassium Thiosulphate.

The **crystals** of the tritahydrate are four-sided prisms or plates which, according to G. Wyrouboff, belong to the monoclinic system and have the axial ratios $a : b : c = 1·5510 : 1 : 1·2905$; while A. Fock and K. Klüss gave $1·5517 : 1 : 1·2142$, and $\beta = 98° 40'$. O. Döpping said that the monohydrate forms six-sided columns or needles ; and A. Fock and K. Klüss, that the tritapentahydrate furnishes hemimorphic, rhombic pyramids with the axial ratios $a : b : c = 0·8229 : 1 : 1·4372$. G. Wyrouboff also examined these crystals ; he also found the **specific gravity** of the tritahydrate to be 2·230, and the mol. vol. 87·8. O. Döpping found that the monohydrate loses its water at 100°—more rapidly at 150°–160° ; and a similar remark applies to the tritapentahydrate. F. Kessler showed that the crystals of the monohydrate are stable in air, but they effloresce over sulphuric acid or at 40°. C. Pape found that the hydrated salt decomposes rapidly at 200° ; while the dehydrated salt is decomposed at 220° to 225°, without loss of weight, into a mixture of a mol. of the pentasulphide and 3 mols. of sulphate ; if the salt is not completely dehydrated, some sulphur is also formed. C. F. Rammelsberg said that decomposition begins at about 400°, and at 470°, the reaction is : $4K_2S_2O_3 = 3K_2SO_4 + K_2S_5$. L. N. Vauquelin also examined the action of heat on the salt. C. Pape gave 0·197 for the **specific heat** of the anhydrous salt between 20° and 100°. M. Berthelot gave for the **heat of formation,** $(K_2,S_2,3O_{gas}) = 266·48$ Cals. ; and $-4·98$ Cals. for the **heat of solution** of the salt, dried in vacuo, in 90 parts of water at 10° ; and $-2·280$ to $-2·490$ Cals. for the tritapentahydrate at 10°. F. Martin and L. Metz gave 283 Cals. for the heat of formation of $K_2S_2O_3$. J. B. Austin discussed the heat of hydration. V. J. Sihvonen found maxima in the **reflection ultra-red spectrum** at $9·1\mu$, $10·2\mu$, $15·2\mu$, and $19·5\mu$. C. Pape gave 8·39 for the rotary polarization of the crystals.

G. S. Kirchhoff found that the salt is odourless, and has at first a cooling taste which afterwards becomes bitter. Though the salt is stable in air, G. S. Kirchhoff observed that if the soln. containing free alkali is exposed to **air,** it is converted into sulphite and sulphate. W. Spring showed that the salt is reduced by **sodium-amalgam** to sulphide ; and H. Debus, that with a great excess of **sulphurous acid** no precipitation of sulphur occurs, but a yellow liquid is produced containing thiosulphuric acid ; if a smaller proportion of sulphurous acid is used, sulphur is precipitated, and tri-, tetra-, and penta-thionates are formed. F. Förster and R. Vogel prepared **potassium sulphurylthiosulphate,** $K_2[S_2O_3(SO_2)]$, and **rubidium sulphurylthiosulphate,** $Rb_2[S_2O_3(SO_2)]$, by the action of liquid sulphur dioxide on the anhydrous thiosulphate at a low temp. The yellow solids with water give clear yellow soln. : $[S_2O_3(SO_2)]'' \rightleftharpoons SO_2 + S_2O_3''$. G. S. Kirchhoff found that the salt is insoluble in **alcohol**; J. L. Casaseca, that it is insoluble in ethyl acetate; and E. Mathieu Plessy, that it is not decomposed by dil. **acetic acid.** G. S. Kirchhoff showed that the aq. soln. dissolves some **metal oxides**—*e.g.* those of copper, silver, mercury, and arsenic. For other reactions, *vide* thiosulphuric acid, and sodium thiosulphate. G. S. Forbes and co-workers studied the induction period in the reaction—clock reaction—between sodium thiosulphate and arsenite (*q.v.*); and M. Meyer, that in the reaction between the thiosulphate and potassium antimonite (*q.v.*).

J. Meyer and H. Eggeling obtained **rubidium thiosulphate,** $Rb_2S_2O_3.2H_2O$, from soln. of rubidium carbonate and barium thiosulphate. The crystals are hygroscopic, and freely soluble in water. C. Chabrié obtained small needle-like crystals of **cæsium thiosulphate,** $Cs_2S_2O_3$, by boiling a mixture of equal parts of flowers of sulphur and cæsium sulphite in twice its weight of water, for nearly an hour—replacing the volatilized water from time to time, and evaporating the filtered liquid in vacuo or over sulphuric acid. The salt is freely soluble in water. J. Meyer and H. Eggeling obtained the dihydrate in hygroscopic, indefinite crystals from the soln. obtained by adding cæsium carbonate to one of barium thiosulphate.

E. Schwicker found that when a conc. soln. of potassium hydrosulphite is sat. with sodium carbonate, and the product is treated with a freshly prepared conc. soln. of ammonium pentasulphide until a permanent yellow coloration is produced, the ammonia expelled by boiling, and the filtered soln. evaporated on a water-bath, transparent plates of **sodium potassium thiosulphate,** $SNa.SO_2.OK.2H_2O$, are formed. The salt is freely soluble in water—213·7 per cent. being dissolved at 15°. It melts at 57°, and when heated with an aq. soln. of ethyl bromide, it yields colourless crystals of potassium ethyl thiosulphate. By treating a conc. soln. of sodium hydrosulphite, sat. in like manner with potassium carbonate, colourless plates of **potassium sodium thiosulphate,** $SK.SO_2.ONa.2H_2O$, melting at 62° are produced. Water dissolves 105·3 per cent. of the salt at 15°. When heated with an aq. soln. of ethyl bromide, sodium ethyl thiosulphate is formed which crystallizes from dil. alcohol in transparent needles which contain a mol. of water. C. Pape obtained **potassium sodium chlorothiosulphate,** $K_2S_2O_3.NaCl$, from a soln. containing the component salts.

J. F. W. Herschel[4] obtained a blue soln. of cuprous thiosulphate by treating a soln. of calcium thiosulphate with copper sulphate or carbonate. C. von Hauer gradually mixed a cold sat. soln. of sodium thiosulphate with a conc. soln. of copper sulphate until the soln. is intensely yellow—rather less than a mol of $CuSO_4$ is needed per mol of $Na_2S_2O_3$; when the soln. is allowed to stand, or warmed a little, crystals are obtained which are washed successively with water, and alcohol, and dried over sulphuric acid. The composition corresponds with impure **cuprous tetrahydrothiosulphate,** $Cu_2O.3S_2O_2.2H_2O$, or $Cu_2H_4(S_2O_3)_3$. If the yellow soln. be exposed to sunlight, or heated over 50°, it forms cupric sulphide; if the precipitate be allowed to stand too long it may turn brown. C. and I. Bhaduri said that the yellow soln. begins to darken at 35°–40°. The excess of cupric sulphate used forms a complex salt with the sodium salt. C. and I. Bhaduri, and G. Vortmann found that the product is always contaminated with sodium thiosulphate. C. and I. Bhaduri obtained the salt by heating cuprous hydroxide with a soln. of sodium thiosulphate. C. von Hauer found that the golden-yellow microscopic crystals when heated out of contact with air furnish water, sulphur dioxide, and sulphuric acid; a sublimate of sulphur; and a residue of cupric sulphide. The thiosulphate is sparingly soluble in water; but it readily dissolves in soln. of ammonium chloride, and of sodium thiosulphate. C. von Hauer, and C. and I. Bhaduri showed that the soln. in sodium thiosulphate soon decomposes, forming copper sulphide. The salt forms colourless liquids with ammonia and ammonium carbonate soln., and when exposed to air they become blue, while that in ammonia deposits a blue, crystalline salt. Nitric acid dissolves the salt, red fumes are evolved, and sulphur is deposited; with hydrochloric acid, sulphur is deposited and hydrogen sulphide is given off.

G. Arthaud found that a mixed soln. of sodium thiosulphate, copper sulphate, and tartaric acid decomposes urea quantitatively.

A. Rosenheim and S. Steinhäuser made yellow prisms of **ammonium cuprous thiosulphate,** $(NH_4)_2S_2O_3.Cu_2S_2O_3.2H_2O$, or $(NH_4)CuS_2O_3.H_2O$, from a soln. of a mol of cupric sulphate and 2 mols of ammonium thiosulphate, or from a soln. of the trithiosulphate and cupric sulphate. Also **ammonium cuprous trithiosulphate,** $2(NH_4)_2S_2O_3.Cu_2S_2O_3.1\frac{1}{2}H_2O$, by mixing a cold, conc. soln. of cupric sulphate with ammonium thiosulphate until the liquid is yellow—a mol of $CuSO_4$ requires 3 or 4 mols of $(NH_4)_2S_2O_3$. If too much ammonium salt is used, evaporation in the desiccator colours the soln. brown. The white needles are washed with cold water, alcohol, and ether, and dried on a porous tile. The salt is readily dissolved by water, but is insoluble in alcohol; it slowly gives off ammonia; and is decomposed by exposure to air or by heat forming copper sulphide. H. Bassett and R. G. Durrant reported **ammonium cuprous pentathiosulphate,** $2Cu_2S_2O_3.3(NH_4)_2S_2O_3.H_2O$, to be formed from conc. soln. of copper nitrate and ammonium thiosulphate. A. Ferratini found that **hydrazine cuprous thiosulphate,** $(N_2H_4)_2H_2S_2O_3.Cu_2S_2O_3.1\frac{1}{2}H_2O$, can be prepared from cuprous chloride and hydrazine thiosulphate; the salt does not melt when heated up to 250°. J. Meyer and H. Eggeling mixed soln. of cupric sulphate and of **lithium cuprous thiosulphate,** and found that the soln. is first decolorized, and then coloured green and finally yellow. It is assumed that an unstable soln. of lithium thiosulphate is formed, but the salt cannot be isolated; it decomposes in the cold, forming copper sulphide and sulphate, lithium sulphate, and sulphur dioxide. Only decomposition products are obtained by evaporating in vacuo over sulphuric acid, a sat. soln. of cuprous iodide in a conc. soln. of lithium thiosulphate.

A soln. of copper sulphate is decolorized by sodium thiosulphate, for the soln. becomes successively brown, green, yellowish-green, and yellow. It is supposed that a complex **sodium cuprous thiosulphate** is formed. If an acid be present, cuprous sulphide is formed; and if the soln. be boiled, cupric sulphide. If a mixture of the two salts be heated in a sealed tube, at 140°–200°, J. T. Norton observed that cuprous and cupric sulphides, and sulphur are produced. In the presence of air, the soln. of sodium cuprous thiosulphate slowly decomposes with the formation of sodium tetrathionate and hydrated cuprous oxide, but in the presence of sulphuric acid, the precipitation of the copper proceeds more slowly, for the hydrated cuprous oxide dissolves so long as any free acid is present. In the presence of air, the hydrated cuprous oxide is oxidized to the cupric state which does not dissolve in the soln. The addition of calcium or sodium hydroxides to the soln. may precipitate hydrated cuprous oxide, but this passes into soln. on adding more sodium thiosulphate; the addition of sodium carbonate has no action below 30°, but at that temp., cuprous carbonate is precipitated, and it too dissolves on adding more sodium thiosulphate. The reaction between sodium thiosulphate and soln. of copper salts was studied by A. Bernthsen, H. Bollenbach, E. Crouzel, F. J. Faktor, J. de Girard, C. Himly, J. Meyer, H. Rose, P. Schützenberger and C. Risler, G. Vortmann, and J. W. Westmoreland. The application of the reaction between copper salts and sodium thiosulphate to analytical work was examined by A. Carnot, E. Fleischer, J. de Girard, C. Himly, H. Nissenson and B. Neumann, A. L. Orlowsky, H. Vohl, G. Vortmann, and M. Willenz. Among the by-products of the reaction, F. Kessel noted sulphites; F. Kessel, C. F. Rammelsberg, J. J. von Renesse, M. Sievert, G. Vortmann, and E. Zettnoff, tetrathionates; and M. Sievert, sulphuric acid. A freshly prepared soln. of sodium cuprous thiosulphate—obtained by mixing soln. of sodium thiosulphate and copper sulphate—is employed in the extraction of gold and silver from sulphide ores—either simple or in combination with arsenic and antimony sulphides. It can also be used with ores containing metallic silver. The soln. of silver is treated with sodium sulphide and the precipitated sulphide is worked for silver and copper sulphides. A soln. of sodium cuprous thiosulphate can be obtained which will dissolve silver nine times as rapidly as a soln. of ordinary sodium thiosulphate; on the other hand, silver chloride is dissolved more slowly by the sodium copper thiosulphate. Gold is not dissolved by the sodium cuprous thiosulphate soln. any more rapidly than a soln. of ordinary sodium thiosulphate. A soln. of calcium thiosulphate is not so good for the purpose because if lead is present, it is precipitated by the addition of sodium carbonate, and with calcium thiosulphate, calcium carbonate would also be precipitated. The enhanced solvent power of sodium cuprous thiosulphate is attributed to the greater solvent power of the copper salt for oxygen which is carried to the silver. Silver sulphide is rapidly decomposed by the soln. with the precipitation of copper sulphide and the dissolution of the silver. C. and I. Bhaduri found that cuprous oxide dissolves in sodium thiosulphate when gently warmed according to the equation $Cu_2O+H_2O+Na_2S_2O_3=2NaOH+Cu_2S_2O_3$. The copper thiosulphate is held in soln. by an excess of sodium thiosulphate. Under ordinary conditions, this soln. is very unstable, and quickly deposits copper sulphide.

Numerous complexes of sodium and cuprous thiosulphates have been isolated, but, as emphasized by A. Rosenheim and S. Steinhäuser, and by W. Muthmann and L. Stützel, it is not clear if complex salts are formed, or if isomorphous mixtures, whose composition depends on the temp. and conc. of the soln., are involved. The salts are not very soluble, and readily decompose in soln. G. Sambamurty studied the period of induction in the formation of cuprous sulphide from sodium cuprous thiosulphate. J. de Girard reported **sodium cuprous pentathiosulphate,** $2Na_2S_2O_3.3Cu_2S_2O_3$, to be formed by the action of cold soln. with 8 mols of sodium thiosulphate, and 6 mols of copper sulphate. The *pentahydrate* was obtained by C. Lenz by mixing a soln. of sodium thiosulphate with an excess of copper sulphate, filtering rapidly, washing with dil. acetic acid, and drying in vacuo over sulphuric acid; E. Crouzel precipitated the salt from its soln. by adding alcohol. C. A. Stetefeldt, and E. H. Russell observed that some sulphuric acid is formed during the reaction. G. Vortmann made the salt by washing the octohydrate with water and alcohol, and drying in a desiccator. H. Bassett and R. G. Durrant said that the salt is the *hexahydrate.* G. Vortmann obtained lemon-yellow crystals of the *octohydrate* from a soln. of 1–2·5 mols of cupric sulphate, and 2 mols of sodium thiosulphate kept at about 40°. The salt is filtered from the warm soln., washed with water, and dried in air. J. de Girard obtained it in a similar way at 45°. C. Lenz said that the pentahydrate is sparingly soluble in water; and E. H. Russell, that 100 parts of water dissolve 0·284 part of salt. The aq. soln. is stable up to 85°. C. Lenz found that cold hydrochloric acid gives a white precipitate without evolution of sulphur dioxide, but with the hot acid, sulphur dioxide, cupric sulphide, and a cuprous salt are formed; conc. sulphuric acid decomposes the salt; warm dil. sulphuric acid gives sulphur dioxide and cupric oxide; aq. ammonia forms a yellowish-brown soln. which becomes blue in air. The salt is insoluble in alcohol, and alcohol precipitates from the aq. soln. a salt soluble in water. The salt is freely soluble in a soln. of sodium thiosulphate; and E. H. Russell found that 100 c.c. of 5, 7·5, and 10 per cent. soln. of the sodium thiosulphate dissolve respectively 12·28, 17·46, and 22·54 grms. of the complex salt. E. H. Russell also found that silver sulphide decomposes the salt precipitating cupric sulphide; and that silver chloride dissolves more slowly than in a soln. of sodium thiosulphate alone. E. Crouzel obtained a chocolate-brown precipitate with potassium ferrocyanide—the precipitate is grey with sodium thiosulphate alone. H. Bassett and R. G. Durrant added that cupric salts are reduced at once to the cuprous state on adding excess of sodium thiosulphate; from normal or more conc. soln., the yellow salt, $3Cu_2S_2O_3.2Na_2S_2O_3.6H_2O$, crystallizes out rapidly. Sodium tetrathionate is simultaneously produced. When copper nitrate is used, pure specimens of the yellow salt are obtained. With copper sulphate, the yellow salt contains $3Cu_2SO_4.2Na_2SO_4.6H_2O$ in solid soln. With copper chloride, the yellow salt soon gives place to the white salt, $Cu_2S_2O_3.Na_2S_2O_3.H_2O$ (*vide infra*), which invariably contains $Cu_2Cl_2.2NaCl.H_2O$ in solid soln. The yellow salt in this case was found to be a mixture containing some of the white salt. The pure yellow salt is quite stable if kept dry and prepared perfectly free from adhering tetrathionate. When strongly heated, it yields cuprous sulphide and sodium sulphate, whilst sulphur, sulphur dioxide, and water are expelled. P. Jochum made *hexahydrated* **sodium cuprous decathiosulphate,** $4Na_2S_2O_3.5Cu_2S_2O_3.6H_2O$, by treating sodium cuprous trithiosulphate with a soln. of sodium thiosulphate; and the *octohydrate,* by adding a cold, sat. soln. of sodium thiosulphate to a cold, conc. soln. of copper sulphate until a green colour appears; A. Benrath obtained the *enneahydrate;* and A. Rosenheim and S. Steinhäuser, the *hemiheptadecahydrate,* by mixing soln. of the component salts in theoretical proportions. P. Jochum prepared *monohydrated* **sodium cuprous dithiosulphate,** $Na_2S_2O_3.Cu_2S_2O_3.H_2O$, or $NaCuS_2O_3.\frac{1}{2}H_2O$, as a yellow, amorphous mass, from soln. of sodium thiosulphate and cuprous chloride as free as possible from acid; H. Bassett and R. G. Durrant said that the salt is monohydrated—*vide supra.* E. H. Russell, and C. A. Stetefeldt prepared the *dihydrate,* by the action of soln. of 2 parts of sodium thiosulphate and one part of copper sulphate. Some penta- and tri-thionates are formed at the same time. A. Rosenheim and S. Steinhäuser obtained the same hydrate by adding sodium thiosulphate to a conc. soln. of copper sulphate until it is decolorized, and then adding copper sulphate until the liquid is yellow. The salt is insoluble in water, and in alcohol. C. and I. Bhaduri made the *hemipentahydrate* by mixing conc. soln. of sodium thiosulphate and copper sulphate or acetate in the molar proportion 2 : 1, adding a large excess of acetic acid, and washing the yellowish-white precipitate with dil. alcohol. G. Vortmann, and J. de Girard reported the *trihydrate* to be formed by mixing cold soln. of a mol of copper sulphate (1 : 2·5) and 2 mols of sodium thiosulphate (2 : 2) at the ordinary temp. A great many copper salts with copper thiosulphate have been reported, but it is highly probable that many of them are solid soln. A. Benrath found that the composition of the solid phase in soln. of the two salts varies with the amount of the sodium salt in soln. The results are shown in Fig. 123, and the break in the curve corresponds with **sodium cuprous dithiosulphate,** $Na_2S_2O_3.Cu_2S_2O_3.2H_2O$; or $CuNaS_2O_3.H_2O$, or $Na_2[Cu_2(S_2O_3.H_2O)_2]$, and it forms an indefinite number of solid soln. with sodium thiosulphate, and it is miscible with cuprous thiosulphate up to the formation of $4Na_2S_2O_3.5Cu_2S_2O_3.9H_2O$. Gaseous ammonia converts the salt $Na_2S_2O_3.Cu_2S_2O_3.2H_2O$ into **sodium cuprous diamminodithiosulphate,** $Na_2S_2O_3.Cu_2S_2O_3.2NH_3$. G. Bhaduri passed acetylene into a soln. of sodium thiosulphate and copper acetate and obtained a red precipitate of sodium cuprous acetylidothiosulphate, $5Na_2S_2O_3.5Cu_2S_2O_3.5Cu_2C_2.C_2H_2.10H_2O$. This product dissolves in water, but may be washed with alcohol. It forms a brick-red powder, which burns like gunpowder when heated. It decomposes slowly at 33°, or in ten hours on the water-bath. The red soln. is decolorized by acids; the colour is restored on adding alkali immediately, but not after a short time. Alkalies, except ammonia, precipitate a brown explosive substance.

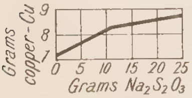


FIG. 123.—Solubility of Cuprous Thiosulphate in Solutions of Sodium Thiosulphate.

C. and I. Bhaduri made yellow crystals of **sodium cuprous dodecathiosulphate,** $5Na_2S_2O_3.7Cu_2S_2O_3.16H_2O$, by mixing sat. soln. of copper sulphate this and sodium thiosulphate in the molar proportion 1 : 2, and at 20°–34°, and by mixing soln. of copper acetate and sodium thiosulphate in almost any proportion. A. Rosenheim and S. Steinhäuser made yellow crystals of *hexahydrated* **sodium cuprous heptathiosulphate,** $3Na_2S_2O_3.4Cu_2S_2O_3.6H_2O$, from a yellow soln. obtained by adding sodium thiosulphate to a conc. soln. of copper sulphate; and C. and I. Bhaduri, the *enneahydrate,* by mixing sat. soln. of the component salts at 50°–60°. G. Vortmann reported **sodium cuprous trithiosulphate,** $2Na_2S_2O_3.Cu_2S_2O_3.4H_2O$, to be formed by adding the calculated quantity of sodium thiosulphate to a soln. of the pentathiosulphate; he similarly obtained *dihydrated* **sodium cuprous tetrathiosulphate,** $3Na_2S_2O_3.Cu_2S_2O_3.2H_2O$, and the same salt was reported by C. Lenz, and C. F. Rammelsberg; and P. Jochum reported the *hexahydrate* to be formed by adding alcohol to the colourless soln. obtained by mixing soln. of the component salts. P. Jochum also reported dihydrated **sodium cuprous enneathiosulphate,**

$7Na_2S_2O_3.2Cu_2S_2O_3.2H_2O$, by adding sodium thiosulphate to a soln. of the dithiosulphate in one of sodium sulphate until the liquid is colourless; if alcohol be added, the *dodecahydrate* is formed. F. Kessel said that **sodium cuprous pentathiosulphate,** $4Na_2S_2O_3.Cu_2S_2O_3.6H_2O$, is formed by mixing a soln. of sodium thiosulphate with an excess of copper sulphate or acetate at −10°. G. Vortmann also prepared this salt by adding the calculated quantity of sodium thiosulphate to a soln. of the pentathiosulphate.

O. L. Shinn reported **ammonium sodium cuprous hexamminoctothiosulphate,** $(NH_4)_2S_2O_3.4Na_2S_2O_3.3Cu_2S_2O_3.6NH_3$, in blue, tetragonal crystals, by adding a conc. aq. soln. of sodium thiosulphate to an ammoniacal soln. of a copper salt, or to an ammoniacal soln. of cuprous oxide. When dry the salt is fairly stable in air, but it rapidly oxidizes when moist, and is partly decomposed by water. According to A. Rosenheim and S. Steinhäuser, the halide salts of the first group of the periodic system are alone capable of forming complex salts with the alkali or ammonium thiosulphates which are analogous to the complex salts of potassium iodide and ethyl sulphonates of the type $RI.4(C_2H_5)RSO_3$. They are said to be true compounds, and they can be re-crystallized from water without decomposition. They are made by saturating a soln. of ammonium thiosulphate with silver or cuprous halide, and concentrating the soln. over sulphuric acid in vacuo. With cuprous chloride, **ammonium cuprous dichlorotetrathiosulphate,** $NH_4Cl_{0\cdot4}(NH_4)_2S_2O_3.CuCl$, is formed in tetragonal crystals with the axial ratio $a:c=1:0\cdot63177$; with cuprous bromide, **ammonium cuprous dibromotetrathiosulphate,** $NH_4Br_{0\cdot4}(NH_4)_2S_2O_3.CuBr$, in tetragonal crystals with $a:c=1:0\cdot63828$; **ammonium cuprous dithiocyanatotetrasulphate,** $NH_4CyS.4(NH_4)_2S_2O_3.CuCyS$. With cuprous iodide, **ammonium cuprous diiodotetrathiosulphate,** $NH_4I_{0\cdot4}(NH_4)_2S_2O_3.CuI$, in tetragonal crystals with the axial ratio $a:c=1:0\cdot6341$. E. Brun also prepared this compound by mixing a large excess of a 50 per cent. soln. of ammonium thiosulphate with powdered cuprous iodide, or a soln. of it in ammonium iodide. The salt is stable at ordinary temp., decomposes slowly at 100°, and at higher temp. gives off sulphur and its dioxide, iodine, and ammonia. A soln. of the salt decolorizes iodine with the precipitation of cuprous iodide; and when boiled with water it is decomposed with the deposition of cuprous sulphide. E. Brun also reported that if a smaller proportion of ammonium thiosulphate is used, the salt $7(NH_4)_2S_2O_3.Cu_2S_2O_3.8CuI.4H_2O$, or **ammonium tetraiodothiosulphate,** $(NH_4)_7(S_2O_3)_4.4CuI.2H_2O$, is formed in yellow needles; and if an excess of sodium thiosulphate is avoided, **ammonium diiodothiosulphate,** $(NH_4)_2S_2O_3.2CuI.H_2O$, is formed in insoluble yellow needles. A. Rosenheim and S. Steinhäuser could not verify the existence of these two compounds, but they obtained *ammonium cuprous cyanidothiosulphate and thiocyanatothiosulphate* analogous to the corresponding halides. G. Canneri and R. Luchini prepared a series of complex salts by dissolving in fused sodium thiosulphate freshly prepared cuprous halides, or thiocyanate. They form white crystals not affected by light, and give clear, colourless, aq. soln. These compounds are **sodium cuprous chloropentathiosulphate,** $CuCl.5Na_2S_2O_3$, or $Na_{10}[ClCu(S_2O_3)_5]$; **sodium cuprous bromopentathiosulphate,** $CuBr.5Na_2S_2O_3$, or $Na_{10}[BrCu(S_2O_3)_5]$; **sodium cuprous bromodecathiosulphate,** $CuBr.Cu_2S_2O_3.9Na_2S_2O_3$, or $Cu_2Na_{18}[BrCu(S_2O_3)_{10}]$; **sodium cuprous iodobromopentathiosulphate,** $CuBr.5Na_2S_2O_3.NaI$, or $CuNa_{11}[IBrCu(S_2O_3)_5]$; and **sodium cuprous dithiocyanatopentathiosulphate,** $2CuCyS.5Na_2S_2O_3$, or $CuNa_{10}[(CyS)_2(S_2O_3)_5]$. The co-ordination formulæ, added G. Canneri and R. Luchini, cannot, however, be supported by experimental data other than the colour of the salts, this indicating that the cuprous ion forms part of a complex radicle constituted of groupings in such condition that they exhibit increased resistance to react with their specific reagents. Water has a dissociating action on these complex compounds.

A. Rosenheim and S. Steinhäuser reported that **sodium cuprous dichlorotrithiosulphate,** $2Na_2S_2O_3.Cu_2S_2O_3.2CuCl$, is produced as a white crystalline precipitate, by the action of conc. aq. soln. of 2 mols of sodium thiosulphate on 4 mols of cuprous chloride; C. and I. Bhaduri, **sodium cuprous octochlorotetradecathiosulphate,** $5Na_2S_2O_3.9Cu_2S_2O_3.8NaCl$, as a white pulverulent mass, by the action of a sat. soln. of sodium thiosulphate on one of cupric chloride; and M. Siewert, **sodium cuprous tetrachloropentathiosulphate,**

$2Na_2S_2O_3.3Cu_2S_2O_3.4NaCl.8H_2O$, as a white amorphous mass, by the action of a sodium thiosulphate soln. on sodium cuprous chloride. F. Kessel made **sodium cuprous dithiosulphatosulphide,** $Na_2S_2O_3.Cu_2S_2O_3.CuS.4H_2O$, from a cold soln. of sodium thiosulphate and an excess of copper sulphate or acetate, kept at about 0° for some time. The salt was also studied by C. Lenz, M. Siewert, J. J. van Renesse, C. and I. Bhaduri, and H. Peltzer. By dissolving the complex salt in hydrochloric acid, and adding alcohol, F. Kessel obtained **sodium cuprous dithiosulphatodisulphide,** $Na_2S_2O_3.Cu_2S_2O_3.2CuS$; and if the soln. in conc. hydrochloric acid be dried in a desiccator at 0°, a dark brown **sodium cuprous chlorodithiosulphatosulphide** is formed. P. Jochum obtained yellow needles of **sodium cuprous disulphatoctothiosulphate,** $3Na_2S_2O_3.5Cu_2S_2O_3.2Na_2SO_4.H_2O$, by adding a cold, conc. soln. of sodium thiosulphate to a conc. soln. of copper sulphate until a yellow colour is developed, and allowing the liquid to stand for 24 hrs. E. Brun reported *potassium and sodium iodothiosulphates* can be formed analogous to the ammonium salts.

W. Muthmann and L. Stützel obtained evidence of the formation of **potassium cupric thiosulphate,** $K_2S_2O_3.CuS_2O_3$, or $Cu(KS_2O_3)_2$, by mixing soln. of cupric sulphate and potassium thiosulphate; when the blue colour is changed to yellow, the soln. furnishes slender, colourless needles, which become brown if allowed to remain in contact with the mother-liquid a few days. It is probable that this salt is the same as the $Cu_2S_2O_3.2K_2S_2O_3$, prepared by J. B. Cohen; and that the latter is really a cupric salt. Soda-lye produces a very faint turbidity in the aq. soln., whilst the solid substance, on digestion with this reagent, yields black copper oxide; potassium ferrocyanide gives the characteristic reddish-brown cupric ferrocyanide, and hydrogen sulphide produces colloidal cupric sulphide, which is precipitated by acids and neutral salts. C. F. Rammelsberg prepared **potassium cuprous dithiosulphate,** $K_2S_2O_3.Cu_2S_2O_3.2H_2O$, in yellow crystals, by allowing a green soln. of potassium thiosulphate and copper sulphate or acetate to stand for a few days. A. Rosenheim and S. Steinhâuser also made this salt; and B. Hornig obtained it by leaving a mixture of potassium trithionate and a cold, sat. soln. of copper acetate in the dark for several days. The crystals become brown in air, and when heated become black owing to the formation of cupric sulphide and potassium sulphate free from the sulphide. The salt is insoluble or very sparingly soluble in water; and the aq. soln. decomposes into sulphur dioxide, cupric oxide and potassium sulphate when boiled; hot alkali-lye forms cuprous hydroxide and alkali thiosulphate; the soln. in potassium thiosulphate furnishes white needles of **potassium cuprous trithiosulphate,** $2K_2S_2O_3.Cu_2S_2O_3$. This salt was also prepared by J. B. Cohen from one part of a soln. of cupric sulphate to rather less than 4 parts of potassium thiosulphate in a hot sat. soln. The crystals are washed with a little cold water, and dried in air. W. Muthmann and L. Stützel mixed soln. of 80 grms. of potassium thiosulphate, and 20 grms. of cupric sulphate diluted to a litre, and allowed to stand 24 hrs.; the crystals were dried over sulphuric acid. A. Rosenheim and S. Steinhäuser obtained the salt from a mixture of a mol of copper sulphate and 4 mols of potassium thiosulphate. J. B. Cohen, W. Muthmann and L. Stützel, and A. Rosenheim and S. Steinhäuser reported a *dihydrate*; A. Rosenheim and S. Steinhäuser, and W. Muthmann and L. Stützel, a *trihydrate;* and W. Muthmann and L. Stützel, a *tetrahydrate—vide infra,* potassium cupric thiocyanate. The anhydrous salt does not change its colour at 100°–110°, and suffers no loss in weight; at 120°, J. B. Cohen said that some sulphur dioxide is given off. The salt is freely soluble in water. The aq. soln. remains clear and colourless when soda-lye is added, but the solid salt is quickly blackened by conc. soda-lye; it is coloured blue in a few minutes by ammonia; deep brown by hydrogen sulphide; and reddish-brown by potassium ferrocyanide. It is insoluble in an aq. soln. of potassium thiosulphate; and it is turned brown after 2 or 3 days' contact with this menstruum. A. Benrath examined the mutual solubility of cuprous and sodium thiosulphates in water at 15°, and 35°. The

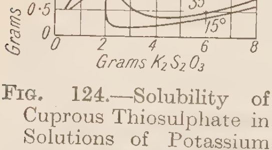


FIG. 124.—Solubility of Cuprous Thiosulphate in Solutions of Potassium Thiosulphate.

results are illustrated by Fig. 124. They found that dihydrated potassium cuprous dithiosulphate, $K_2[Cu_2(S_2O_3.H_2O)_2]$, appears as an unstable greenish-yellow salt at 15° but not at 35°. There is also formed yellow trihydrated potassium cuprous trithiosulphate, $K_2[Cu_2(S_2O_3.H_2O_3)]$, and white anhydrous potassium cuprous trithiosulphate, $K_4[Cu_2(S_2O_3)_3]$. Gaseous ammonia converts it into **potassium cuprous amminotrithiosulphate,** $2K_2S_2O_3.Cu_2S_2O_3.NH_3$. When alcohol is added to the aq. soln., J. B. Cohen said that **potassium cuprous tetrathiosulphate,** $3K_2S_2O_3.Cu_2S_2O_3.3H_2O$, is formed. This salt was obtained by C. F. Rammelsberg by adding alcohol to a sat. soln. of the dithiosulphate, and allowing the oily precipitate to crystallize. It is more soluble than the dithiosulphate. A. Rosenheim and S. Steinhäuser, and W. Muthmann and L. Stützel, doubt the chemical individuality of this salt.

J. Meyer and H. Eggeling obtained **rubidium cuprous dithiosulphate,** $Rb_2S_2O_3.Cu_2S_2O_3.2H_2O$, from soln. of equimolar parts of the component salts; the precipitate is washed with cold water. The yellow crystalline powder is very unstable; and with warm water, cupric sulphide separates out. They also obtained **cæsium cuprous dithiosulphate,** $Cs_2S_2O_3.Cu_2S_2O_3.2H_2O$, from a soln. of one mol of copper sulphate and 3 mols of cæsium thiosulphate. With the molar proportions $Rb_2S_2O_3$ and $CuSO_4$, 2 : 1, J. Mayer and H. Eggeling obtained **rubidium cuprous trithiosulphates,** $2Rb_2S_2O_3.Cu_2S_2O_3.2H_2O$; and with the proportions 3 : 1, **rubidium cuprous tetrathiosulphate,** $3Rb_2S_2O_3.Cu_2S_2O_3.2H_2O$.

The brown colour which is first developed when cold soln. of sodium thiosulphate and copper sulphate are mixed is supposed by G. Vortmann, J. Meyer and H. Eggeling, and P. Jochum to be produced by a very unstable **cupric thiosulphate,** CuS_2O_3. The reducing action on the cupric salt of the thiosulphate prevents the formation of cupric thiosulphate in aq. media. The cupric salt, however, is stabilized by ammination. P. Pudschies obtained dark blue needles of **cupric tetramminothiosulphate,** $CuS_2O_3.4NH_3$, by mixing a soln. of copper acetate in conc. aq. ammonia with sodium thiosulphate, and dark blue cubes by precipitation with alcohol from dil. soln. At 25°, 100 parts of water dissolve 21·79 parts of salt. The mol. electrical conductivities of soln. with a mol of the salt in 4·006, 8·012, and 16·024 litres are respectively 27·7, 24·3, and 40·9. P. Pudschies also measured the partition of ammonia between an aq. soln. of this salt and chloroform. W. Schütte prepared violet needles of **sodium cuprosic tetramminotetrathiosulphate,** $2Na_2S_2O_3.Cu_2S_2O_3.CuS_2O_3.4NH_3$, by adding a conc. soln. of sodium thiosulphate to a warm soln. of a cupric salt, or of cuprous chloride. The salt was also prepared by H. Peltzer, and M. Siewert; while the *dihydrate* was obtained by P. Pudschies. The deep blue salt represented by K. Bhaduri as a trithionate was shown by A. Benrath to be **sodium cuprosic pentamminotetrathiosulphate,**

$$[(Cu_2S_2O_3)Cu(NH_3)_5]^{S_2O_3}_{(Na_2S_2O_3)_2}$$

He said that the deep blue colour makes it unlikely to be solely a cuprous salt. It is considered to be the salt previously made by several workers from sodium thiosulphate and an ammoniacal copper salt soln. The ratio $Cu^{\cdot} : Cu^{\cdot\cdot}$ is 2 : 1. All the sulphur is in the thiosulphate complex; and there are probably five NH_3 mols. present. The cupric atom is considered to be the central atom of the complex. It has not been found possible to prepare analogous compounds with potassium thiosulphate in place of sodium, or with ethylamine or pyridine in place of ammonia. Ethylenediamine gives a violet salt, **copper hemitrisethylenediaminothiosulphate,** $2CuS_2O_3.3C_2H_4(NH_2)_2.2H_2O$, in which the whole of the copper is in the cupric condition. G. T. Morgan and F. H. Burstall prepared **copper bisethylenediaminothiosulphate,** $[Cu\ en_2]S_2O_3$, by double decomposition between barium thiosulphate and copper bisethylenediaminosulphate. The complex thiosulphate remained unchanged in air, but on heating it decomposed without melting at 150°–155°. The stable purplish-blue soln. in water became blue on addition of an aq. soln. of sodium hydroxide, whereas a warm alcoholic soln. of soda precipitated cupric oxide. Silver nitrate gave a white precipitate, blackening rapidly even in the cold. Sulphuric and hydrochloric acids discharged the purplish-blue colour of the soln., in the former case with the formation of a brown precipitate. D. W. Horn and R. E. Crawford prepared **cuprosic amminosulphothiosulphate,** $Cu_{10}S_{15}O_{18}.9NH_3$, or $6CuS_2O_3.Cu_2S.CuS.9NH_3$, by mixing a soln. (sp. gr. 1·26 at 21°) of sodium thiosulphate in conc. aq. ammonia, with a soln. of cupric chloride. The blue crystals of the salt are stable.

According to J. F. W. Herschel:

> If a soln. of silver nitrate be dropped into a dil. soln. of potassium hyposulphate, the white turbidity at first produced disappears on agitation; as the quantity of silver salt added to the soln. increases, grey flakes are produced, and the supernatant liquor acquires a sweet taste owing to the presence of the dissolved silver hyposulphate. The silver is not precipitated from the soln. by sodium chloride, but it does give a precipitate with hydrogen sulphide. If more silver nitrate be added, the precipitate turns brown, and it is afterwards converted into black silver sulphide, and the supernatant liquor no longer tastes sweet, and it gives a precipitate with sodium chloride. On the other hand, if the soln. of potassium hyposulphate be added at once to the quantity of silver nitrate soln. required for its decomposition, the precipitate which is white at first passes successively through pale yellow, greenish-yellow, yellowish-brown, reddish-brown, and to brownish-black—the colour of silver sulphide. A soln. containing only one part of hyposulphate in 97,800 parts of water assumes a brown tint in a few minutes after being mixed with the soln. of silver nitrate.

J. F. W. Herschel, and H. Rose prepared **silver thiosulphate,** $Ag_2S_2O_3$, by adding a dil. soln. of silver nitrate to an excess of sodium thiosulphate, and washing the grey mixture of silver thiosulphate and sulphide with cold water. The thiosulphate was extracted with aq. ammonia, and the soln. just neutralized with nitric acid. The precipitate was dried as rapidly as possible by press. The snow-white powder is sparingly soluble in water. As shown by H. Rose, it readily decomposes: $Ag_2S_2O_3=Ag_2S+SO_3$. According to J. Fogh, the thermal value of this reaction is 20 Cals.; and the heat of formation of $Ag_2S_2O_3$ from $AgNO_3$ and $Na_2S_2O_3$ is 2·6 Cals. Hence the tendency of the newly formed silver thiosulphate to decompose. The reaction $Ag_2S_2O_3+H_2O=Ag_2S+H_2SO_4$ was found by J. Bodnar to be quantitative. The salt is soluble in aq. ammonia, and in soln. of the alkali thiosulphates. According to J. F. W. Herschel, **ammonium silver trithiosulphate,** $2(NH_4)_2S_2O_3.Ag_2S_2O_3$, is precipitated when alcohol is added to a soln. of silver chloride in one of ammonium thiosulphate; the white product is dried in vacuo. If the mother-liquor be evaporated, the same salt is obtained in six-sided prisms with a taste sweet enough perceptibly to flavour 32,000 times its weight of water. It is freely soluble in water. When heated, 100 parts of salt yield 40·62 parts of silver sulphide. If more silver chloride be added to a soln. of ammonium thiosulphate than it is capable of dissolving, the white crystals of **ammonium silver thiosulphate,** $(NH_4)_2S_2O_3.Ag_2S_2O_3$, or $NH_4AgS_2O_3$, are produced. The salt is dried in vacuo. It is insoluble in water, and it turns black when kept in closed vessels, or when heated, giving off sulphur dioxide, and forming silver sulphide. The salt is soluble in aq. ammonia, and is reprecipitated by the addition of acids even if the soln. be very dilute. A. Rosenheim could never obtain a product of constant composition in the attempt to prepare the two compounds reported by J. F. W. Herschel; but a series of mixed salts—*vide infra*—was obtained. A. Rosenheim and G. Trewendt added a soln. of silver nitrate to an ice-cold soln. of alkali thiosulphate, and found that sparingly soluble salts separate out, whilst soluble salts require the addition of alcohol for precipitation. Thus, the salt $NH_4AgS_2O_3$ is sparingly soluble, but **ammonium silver heptathiosulphate,** $(NH_4)_5[Ag_3(S_2O_3)_4]$, is sparingly soluble. A. and L. Lumière and A. Seyewetz said that the ammonium silver sulphide produced when silver bromide is dissolved by a soln. of ammonium thiosulphate is very unstable. A. Ferratini obtained **hydrazine silver thiosulphate,** $(N_2H_4)H_2S_2O_3.Ag_2S_2O_3$, by shaking freshly prepared silver chloride with a soln. of hydrazine thiosulphate. The rectangular crystals become brown at 100°, and melt at 128°–129°. The salt is almost insoluble in water; is reduced slowly by boiling water; is soluble in aq. ammonia; and is attacked by nitric acid.

J. Meyer and H. Eggeling prepared **lithium silver dithiosulphate,** $Li_2S_2O_3.Ag_2S_2O_3.H_2O$, by the action of freshly-precipitated silver chloride on a conc. soln. of lithium thiosulphate. The tabular crystals soon form silver sulphide on exposure to light. They are hygroscopic, and decomposed by boiling water, and by acids. According to A. Rosenheim and S. Steinhäuser, when silver chloride dissolves in a soln. of potassium or sodium thiosulphate, there is a double decomposition resulting in the formation of alkali chloride, and silver thiosulphate. The latter forms complex salts with the excess of sodium thiosulphate. E. Valenta examined the solubility of the silver halides in soln. of sodium thiosulphate. The solubility, *S*, of the silver halide in grams per 100 grms. of soln. for soln. with 100 parts of water and

	$Na_2S_2O_3$ . .	1	5	10	15	20 parts
S	AgCl . .	0·40	2·00	4·10	5·50	6·10
	AgBr . .	0·35	1·90	3·50	4·20	5·80
	AgI . .	0·03	0·15	0·30	0·40	0·60

E. Cohen found that if the sodium thiosulphate be in excess, silver chloride dissolves in accord with $3Na_2S_2O_3+2AgCl=2NaCl+2AgNaS_2O_3.Na_2S_2O_3$; and if the silver salt be in excess, the less soluble $NaAgS_2O_3$ is formed. R. Luther and A. Leubner found that the anion present in the soln. is $Ag(S_2O_3)_2'''$. J. Fogh showed that the decomposition of silver nitrate (2 mols) by sodium thiosulphate (1 mol) with formation of sodium nitrate, silver sulphide, and dissolved sulphuric acid, is complete in four or five minutes, and develops +46 Cals. at 15°. The calculated result is +45·2 Cals. The reaction takes place in two phases, namely, the formation of silver thiosulphate and the decomposition of the latter in presence of water, but the thermochemical disturbances corresponding with each phase could not be determined directly because of the rapidity of decomposition. Calculating from analogy, the heat of formation of silver thiosulphate is +104 Cals., and hence the first phase of the reaction should develop +5·2 Cals., and the second +40 Cals., a result which explains the fact that the decomposition becomes complete without the aid of extraneous energy. The dissolution of silver thiosulphate in excess of a soln. of sodium thiosulphate, develops 34·8 Cals. at 12°. The conversion of silver chloride and bromide into thiosulphate would absorb 13×2 Cals., and $17{\cdot}3\times2$ Cals., and the soln. of these compounds in a soln. of sodium thiosulphate is determined by the formation of the sodium silver thiosulphate. The conversion of silver iodide into thiosulphate would absorb 48·4 Cals., a quantity greater than that developed by the combination of silver thiosulphate and sodium thiosulphate, and hence a soln. of sodium silver thiosulphate yields a precipitate of silver iodide on addition of a soluble iodide, and silver iodide does not dissolve in sodium thiosulphate soln. without the aid of extraneous energy.

E. Müller observed that when silver nitrate is added to a soln. of sodium thiosulphate and the potential between a silver indicator electrode and a normal calomel electrode immersed in the liquid is measured and plotted against the vol. of silver soln. added, a marked deflection in the curve occurs at a point corresponding with the formation of $NaAgS_2O_3$. Further addition of the silver soln. causes the formation of a white precipitate of $Ag_2S_2O_3$, which simultaneously becomes brown, due to decomposition into silver sulphide, and eventually a second deflection in the potential curve occurs at a point a little beyond that corresponding with the formation of $Ag_2S_2O_3$, due to adsorption of silver nitrate by the precipitate. If the titration is carried out at 0°, no decomposition of silver thiosulphate occurs until there is an excess of silver nitrate present, and the second deflection in the potential curve denotes a stoichiometric relation between the reacting substances. In the presence of sodium acetate, the titration may be carried out at 75°, at which temp. the potential change at the end-point is much more marked. There is no indication of the formation of the complex salt, $Na_4Ag_2(S_2O_3)_3$, by the electrometric titration.

J. F. W. Herschel reported crystals of **sodium silver trithiosulphate,** $2Na_2S_2O_3.Ag_2S_2O_3.2H_2O$, to be formed by evaporating a soln. of silver chloride in a soln. of sodium thiosulphate. A. Rosenheim and G. Trewendt used the formula $Na_4[Ag_2(S_2O_3)_3].2H_2O$. A. Rosenheim and S. Steinhäuser used a similar mode of preparation; and C. Lenz obtained it in an analogous way and also by using silver nitrate in place of the chloride; and by precipitation by adding alcohol to the soln. and allowing the oily liquid to crystallize; A. and L. Lumière and A. Seyewetz used silver bromide and alcoholic precipitation. According to C. Lenz, while the evaporation of the aq. soln. furnishes tabular crystals, an alcoholic soln. furnishes acicular crystals. The salt has a very sweet taste; it is stable in air and in light. At 100°, the salt is gradually darkened by the formation of silver sulphide; and a similar product is obtained by the prolonged boiling of the aq. soln. K. Barth obtained silver sulphide, sulphur dioxide, and sulphuric acid by boiling the aq. or acidic soln. Hydrochloric acid slowly decomposes the aq. soln. in the cold. The salt is freely soluble in water, and in aq. ammonia; the salt is soluble in aq. alcohol. J. F. W. Herschel, A. Rosenheim and S. Steinhäuser, and E. Cohen obtained **sodium silver thiosulphate,** $Na_2S_2O_3.Ag_2S_2O_3$, or $NaAgS_2O_3$, or $Na[Ag(S_2O_3)]$, from a soln. of silver chloride to a soln. of sodium thiosulphate; on evaporation, the first crop of crystals may contain the trithiosulphate. C. Lenz obtained it by adding neutral silver nitrate soln. to one of sodium thiosulphate so long as a precipitation occurs. A. Rosenheim and S. Steinhäuser failed to confirm this. A. Schwicker evaporated over sulphuric acid a mixture of sodium thiosulphate and an ammoniacal soln. of a silver salt. A. and L. Lumière and A. Seyewetz, and C. Lenz obtained a *monohydrate;* and the former also a *dihydrate* by allowing the filtrate from a soln. of 150 grms. of crystalline sodium thiosulphate and 58 grms. of silver chloride to stand in darkness. A. Steigmann studied the reduction of sodium silver thiosulphate by sodium hyposulphite, and found the reduction occurs more rapidly in alkaline than in neutral soln., since neutral soln. became acidic owing to the decomposition of the hyposulphite $2Na_2S_2O_4=Na_2S_2O_5+Na_2S_2O_3$; and $Na_2S_2O_5+H_2O=2NaHSO_3$. The silver from alkaline soln. coagulates more rapidly than the blackish-blue silver from acidic soln., which sediments very slowly and yields a precipitate which is deep black in colour. The silver from alkaline soln. is greyish-black, and when rubbed on paper takes on a bronze appearance. The reduction occurs much more rapidly in the presence of a little potassium iodide than in alkaline soln., and more rapidly still in alkaline soln. containing a little potassium iodide. In all cases, the reduced silver is at first colloidal, which rapidly coagulates. In the alkaline soln., the sol remains yellowish-brown in colour until coagulation sets in, but in all other cases the sol becomes reddish-blue very rapidly. The white, tabular crystals of the anhydrous salt were found by A. Schmidt to be monoclinic with the axial ratios $a:b:c=0\cdot6324:1:0\cdot5716$, and $\beta=90° 37'$. The optic axial angle $2V=90° 11'$ for Li-light. The optical character is negative. A. and L. Lumière and A. Seyewetz found that the salt blackens at 60°. The other observers found that the salt is sparingly soluble in cold water, and is decomposed by hot water; it is freely soluble in aq. ammonia; and in an aq. soln. of sodium thiosulphate; dil. hydrochloric acid forms no silver chloride, but with hot soln., silver sulphide is precipitated. A. Rosenheim and G. Trewendt prepared the **sodium silver tetrathiosulphate,** $Na_5[Ag_3(S_2O_3)_4].3H_2O$, as a freely soluble salt, by the method indicated above. A. Schwicker said that the **sodium silver monamminothiosulphate,** $NaAgS_2O_3.NH_3$, is formed by adding alcohol to a mixture of sodium thiosulphate with an ammoniacal soln. of a silver salt. This salt was also made by J. Meyer and H. Eggeling. P. Jochum reported **sodium silver heptathiosulphate,** $6Na_2S_2O_3.Ag_2S_2O_3.21H_2O$, from a sat. soln. of silver chloride in a conc. aq. soln. of sodium thiosulphate; but this has not been confirmed.

J. F. W. Herschel precipitated a potassium silver thiosulphate by adding potassium hydroxide, or a potassium salt to a soln. of silver chloride and sodium thiosulphate. A. Rosenheim and S. Steinhäuser obtained **potassium silver octothiosulphate,** $5K_2S_2O_3.3Ag_2S_2O_3$, by boiling a soln. of silver nitrate and potassium thiosulphate for 15 minutes, making the liquid feebly alkaline with potassium carbonate, and allowing the filtrate to crystallize. E. Jonsson also obtained long, colourless prisms of this salt. The prismatic needles are sparingly soluble in water. J. Meyer and H. Eggeling obtained **potassium silver amminoctothiosulphate,** $5K_2S_2O_3.3Ag_2S_2O_3.NH_3$, in white needles, from an ammoniacal soln. of 1·7 grms. of silver nitrate, and 2 grms. of potassium thiosulphate in a little water. E. Jonsson said that the ability to form additive compounds seems to depend on the presence of unused subsidiary valencies of the silver atom and is most marked in compounds of the type $K_2S_2O_3.Ag_2S_2O_3$; it is scarcely noticeable in the case of the salts $2M_2S_2O_3.Ag_2S_2O_3$ and $5M_2S_2O_3.3Ag_2S_2O_3$. He confirmed the existence of the colourless and yellow alkali silver thiosulphates observed by J. Meyer and H. Eggeling, but doubted whether their isomerism is explicable by assigning the respective formulæ $AgS.SO_2.OK$ and $KS.SO_2.OAg$, since their behaviour towards ethyl iodide indicates that the silver is attached to the sulphur atom in each case. The conversion is brought about by cautiously warming with water, but too drastic treatment leads to the formation of silver sulphide, sulphur dioxide, and sulphate. It appears, therefore, that the yellow compounds are intermediate products in the decomposition of the colourless salts, and the transformation is possibly explained by such a scheme as: $KO.SO_2SAg \rightarrow KO.S.SO_2.Ag$. E. Jonsson prepared **potassium silver tritamminothiosulphate,** $3KAgS_2O_3.NH_3.2H_2O$. J. B. Cohen reported **potassium silver trithiosulphate,** $2K_2S_2O_3.Ag_2S_2O_3$, from a soln. of two parts of potassium thiosulphate and one of silver nitrate made feebly alkaline with potassium carbonate. A. Rosenheim said that the product is the octothiosulphate; but E. Jonsson obtained colourless prisms of this salt by the action of silver nitrate on potassium thiosulphate in the presence of ammonia. If silver chloride be dissolved in cold conc. soln. of potassium thiosulphate, sparingly soluble **potassium silver tetrathiosulphate,** $3K_2S_2O_3.Ag_2S_2O_3.2H_2O$, or $K_3[Ag(S_2O_3)_2].H_2O$, is formed. A. Rosenheim and G. Trewendt obtained **potassium silver tetrathiosulphate,** $K_5[Ag_3(S_2O_3)_4]$, by the method indicated above. A. Schwicker reported potassium silver monamminothiosulphate, $KAgS_2O_3.NH_3$, to be formed by mixing mol. proportions of soln. of potassium thiosulphate and silver nitrate; dissolving the scaly crystals in hot aq. ammonia; and cooling the soln. It was also obtained by adding potassium chloride or sulphate to an aq. soln. of sodium thiosulphate and an ammoniacal soln. of a silver salt.

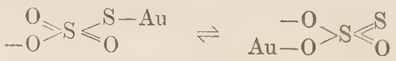
J. Meyer and H. Eggeling prepared **rubidium silver trithiosulphate,** $2Rb_2S_2O_3.Ag_2S_2O_3.3H_2O$, from a soln. of silver chloride and rubidium thiosulphate. The needle-like crystals are not hygroscopic, and are fairly stable in air; they are sparingly soluble in water, and the aq. soln. is decomposed by heat. J. Meyer and H. Eggeling obtained in a similar way **cæsium silver trithiosulphate,** $2Cs_2S_2O_3.Ag_2S_2O_3.3H_2O$. A. Rosenheim and G. Trewendt prepared rubidium silver tetrathiosulphate, $Rb_5[Ag_3(S_2O_3)_4]$, by the method indicated above and found that it forms isomorphous mixtures with the corresponding potassium salt. J. Meyer and H. Eggeling also prepared yellow **rubidium silver amminoheptathiosulphate,** $3Rb_2S_2O_3.4Ag_2S_2O_3.NH_3$; and white **rubidium silver amminodithiosulphate,** $Rb_2S_2O_3.Ag_2S_2O_3.NH_3$.

O. L. Shinn obtained **sodium cuprous silver hexamminoctothiosulphate,** $5Na_2S_2O_3.Cu_2S_2O_3.2Ag_2S_2O_3.6NH_3$, by mixing an aq. soln. of sodium thiosulphate into ammoniacal soln. of silver and copper salts. The tetragonal crystals have the axial ratio $a:c=1:0·8375$. A. Rosenheim and S. Steinhäuser showed that ammonium thiosulphate soln.—unlike the sodium and potassium salts—dissolve silver chloride, forming compounds containing chlorine. They obtained **ammonium silver dichlorotetrathiosulphate,** $NH_4Cl.4(NH_4)_2S_2O_3.AgCl$, by saturating a soln. of ammonium thiosulphate with silver chloride, and concentrating over sulphuric acid in vacuo. The tetragonal crystals have the axial ratio $a:c=1:0·635596$, and are very stable. They can be dissolved without decomposition in cold water or ammonia; they yield a small quantity of silver sulphide when boiled with water. Dil. acids decompose the salt, forming silver chloride and sulphide, sulphur and its dioxide, and hydrogen sulphide; and alkali-lye furnishes silver oxide and ammonia. The crystals of the corresponding **ammonium silver dibromotetrathiosulphate,** $NH_4Br.4(NH_4)_2S_2O_3.AgBr$, are tetragonal with the axial ratios $a:c=1:0·62948$, and are isomorphous with the chloro-salt; **ammonium silver diiodotetrathiosulphate,** $NH_4I.4(NH_4)_2S_2O_3.AgI$, was prepared in a similar way. The same remark applies to the cyanide and thiocyanate. E. Brun also obtained the complex with the ammonium salt and silver iodide and thiosulphate. K. Bhaduri passed acetylene through an ammoniacal soln. of sodium thiosulphate and silver nitrate, and obtained a yellow precipitate which when washed and dried in air, had the composition **sodium silver enneathiosulphate acetylide,** $2Na_2S_2O_3.7Ag_2S_2O_3.18Ag_2C_2.32C_2H_2$. It is soluble in aq. ammonia but reprecipitated by acids; the acid soln. decomposes giving off acetylene and sulphur dioxide. The yellow compound is stable in dry air, but is decomposed by water, forming red **sodium silver henathiosulphate acetylide,** $7Na_2S_2O_3.4Ag_2S_2O_3.86Ag_2C_2.18C_2H_2$.

M. J. Fordos and A. Gélis[6] obtained an acidic soln. of **aurous thiosulphate** by the action of dil. sulphuric acid on barium gold thiosulphate. The soln. can be evaporated in a desiccator to a syrupy liquid having the composition $Au_2S_2O_3.3H_2S_2O_3.nH_2O$. M. Berthelot observed that a yellow, explosive product is produced when acetylene is passed into a soln. of aurous thiosulphate. J. A. Mathews and L. L. Watters showed that the product is aurous carbide. M. J. Fordos and A. Gélis prepared **sodium aurous dithiosulphate,** $Na_3Au(S_2O_3)_2.2H_2O$, by stirring a soln. of one part of auric chloride in 50 parts of water with a soln. of 3 parts of sodium thiosulphate in 50 of water. The mixture is made so slowly that the red liquid becomes colourless before a new addition is made. If an excess of auric chloride is added, auric sulphide is precipitated. The complex salt is precipitated by adding alcohol to the liquid. The salt can be purified by repeatedly dissolving it in water and precipitating it with alcohol. The reaction is represented: $8Na_2S_2O_3+2AuCl_3=3Na_2S_2O_3.Au_2S_2O_3+2Na_2S_4O_6+6NaCl$. J. K. Gjaldbaek, and E. Keiding described the preparation of the salt; and H. Brown recommended the following process:

> A soln. of 41·2 grms. of hydrochloroauric acid in 75 c.c. of water is added, drop by drop, to a 40 per cent. soln. of sodium hydroxide, until the liquid is faintly alkaline to litmus. Gold hydroxide is precipitated. The contents of the beaker are then added to a soln. of 102 grms. of hydrated sodium thiosulphate in 200 c.c. of water while the liquid is being mechanically stirred. After about 5 mins., and while stirring, is added slowly $4N$-HNO_3, from a dropping funnel, at such a rate that the red colour produced by one drop is wholly or nearly discharged before the next drop enters. The red colour is due to the formation of a sodium salt of auric acid. About 45 c.c. of acid are needed. When about half this amount of acid has been added, nearly all the gold hydroxide will have dissolved. When the red colour is no longer produced, the reaction is ended. An excess of acid must be avoided. At the end-point, the soln. is nearly colourless, and is neutral to litmus. Stirring is continued for about 5 mins. until a faint turbidity appears due to sulphur or gold sulphide. The reactions are symbolized $Au_2O_3+4Na_2S_2O_3+2H_2O=4NaOH+2Na_2S_4O_6+Au_2O$; and $Au_2O+4Na_2S_2O_3+H_2O=2NaOH+2Na_3Au(S_2O_3)_2$. The filtered soln. is treated with 4 vols. of alcohol. The white precipitate, contaminated with sulphur, is filtered off, dissolved in the least possible amount of water, filtered, and again treated with alcohol. The treatment can be repeated. Finally, the product is filtered on a suction funnel, and dried in the dark in a vacuum desiccator over sulphuric acid.

H. Möllgaard assumed that the gold is attached to the oxygen as $Au^{\cdots}$, and that it can be prepared only by using gold in the tervalent form. This does not appear to be correct, because K. L. McCluskey and L. Eichelberger prepared this salt by adding a soln. of sodium thiosulphate to a soln. of cæsium chloroaurate: $CsAuCl_4+4Na_2S_2O_3\rightarrow Na_3Au(S_2O_3)_2+Na_2S_4O_6+3NaCl+CsCl$; or sodium chloroaurite: $NaAuCl_2+2Na_2S_2O_3\rightarrow Na_3Au(S_2O_3)_2+2NaCl$. Whether the gold is attached to the oxygen or sulphur cannot be decided, because the salt probably exists in soln. in a tautomeric form:



$$\begin{matrix}O\\-O\end{matrix}{>}S{<}\begin{matrix}S-Au\\O\end{matrix} \rightleftharpoons \begin{matrix}-O\\Au-O\end{matrix}{>}S{<}\begin{matrix}S\\O\end{matrix}$$

The salt is not very stable, but it can be preserved under anhydrous ether in the dark. H. Möllgaard registered this compound by the trade name *sanocrysin*. and studied its relation to what he called the chemotherapy of tuberculosis, A. J. Gelarie and F. R. Greenbaum found that it is not reduced by ferrous chloride or sulphate, oxalic acid, or stannous chloride; in soln., it is decomposed by light. Hydrogen sulphide precipitates auric sulphide. The colourless needles have the composition of the *dihydrate* indicated above; C. Himly said that he obtained a *pentahydrate*. M. J. Fordos and A. Gélis found that the salt has a sweet taste; it is not affected by heat at 100°, but at 150°–160° it loses its water of crystallization without decomposition; at a higher temp., gold and sodium sulphate are formed. The salt is soluble in water; insoluble in alcohol; and sparingly soluble in aq. alcohol; hydrogen sulphide, and soluble sulphides precipitate brown-gold sulphide; iodine tincture in conc. soln. gives no precipitate because of the formation of sodium aurous iodide; but in dil. soln., aurous iodide is precipitated: $2I_2+3Na_2S_2O_3.Au_2S_2O_3=2AuI+2NaI+2Na_2S_2O_6$. Hydrochloric, dil. sulphuric, or organic acids do not precipitate sulphur, nor develop sulphur dioxide; in the cold, nitric acid forms nitric oxide, sulphinic acid, and gold. There is no precipitation of gold with ferrous sulphate, oxalic acid, or stannous chloride. Barium chloride forms the barium salt which is precipitated by alcohol. According to J. K. Gjaldbaek, its aq. soln. is ionized almost entirely into $Na^{\cdot}$ and $Au(S_2O_3)_2'''$ ions; further dissociation into S_2O_3'' and $Au^{\cdot}$ ions takes place only to a very small extent. Attempts to determine the p_H value of the soln. gave results varying from 7·5 to 5·6, the irregularities being ascribed to the presence of impurities. H. Möllgaard discussed the use of this salt in the treatment of tuberculosis; and J. F. Schemberg and C. S. Wright, in the treatment of *lupus erythematosus*. P. Jochum prepared a more complex salt, **sodium aurous heptathiosulphate,** $6Na_2S_2O_3.Au_2S_2O_3.10H_2O$, by adding alcohol to a cold sat. soln. of sodium thiosulphate and a neutral soln. of auric chloride. L. Cassella and Co. also prepared this salt. A. J. Gelarie and F. R. Greenbaum prepared it by slowly adding a conc. soln. of acidic chloride to a conc. soln. of sodium thiosulphate, slowly, and with constant stirring.

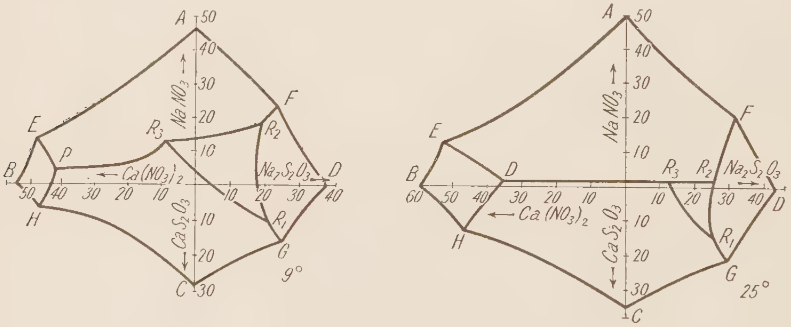
The preparation of **calcium thiosulphate,** $CaS_2O_3.6H_2O$, has been discussed in connection with sodium thiosulphate. Its occurrence in the sulphite liquor of the wood-pulp industry was discussed by R. Sieber.[7] J. F. W. Herschel, and J. Laneau obtained it by boiling a soln. of calcium hydroxide with sulphur, and passing sulphur dioxide into the liquid until it is decolorized; and evaporating the liquid in vacuo or at a low temp.—J. F. W. Herschel said that the temp. should not exceed 60°. E. Kopp obtained it by boiling calcium sulphide with water and sulphur, and treating the soln. with sulphur dioxide as before; H. Müller, by oxidizing a mixture of calcium sulphide and magnesium hydroxide; T. Graham, by oxidizing calcium sulphide in air; and E. Divers and T. Shimidzu added that only a little thiosulphate is formed when air is passed through a soln. of the hydrosulphide; they suggest that hydroxyhydrosulphide is formed by hydrolysis, and that it is the hydrogen sulphide which first oxidizes and the products of the action react with the hydroxyhydrosulphide to form thiosulphate: $Ca(SH)(OH)+2O_2+H_2S=2H_2O+CaS_2O_3$. If the hydrogen sulphide liberated by calcium pentasulphide, in contact with water, is allowed to escape, the remaining tetrasulphide is not oxidized by free oxygen; but if the soln. and air are left in contact in closed vessels, the hydrogen sulphide is oxidized as fast as it is formed, and the oxidation products react with the pentasulphide and sulphur: $CaS_5+2H_2O=Ca(SH)(OH)+3S+H_2S$. E. Divers and T. Shimidzu prefer this formulation of the reaction to $2CaS_5+3O_2=2CaS_2O_3+6S$. E. Donath and F. Müller oxidized the sulphide with manganese dioxide—*vide supra*, sodium thiosulphate. F. Kessler obtained calcium thiosulphate by treating 7 grms. of calcium chloride with a hot, conc. soln. of 8 parts of sodium thiosulphate; sodium chloride separates out as the soln. cools. The liquid is then concentrated at 50° and cooled for the crystallization of the calcium thiosulphate. The reaction $S + CaSO_3.2H_2O \rightleftharpoons CaS_2O_3aq. + 2H_2O$ is a balanced one; and F. R. Bichowsky found the equilibrium conc. at 141°, 122°, 110°, 100°, and 79·8° to be 0·2665, 0·417, 0·618, 0·713, and 1·120 mols per litre respectively with colloidal sulphur above 122°, monoclinic sulphur at 110°–100°, and rhombic sulphur at the lower temp.

$T°$ . .	414°	393°	383°	373°	352°
log K .	—2·971	—2·630	—2·334	—2·221	—1·881

$-68{\cdot}6R \log K = -1945 + 14{\cdot}02T \log T + 0{\cdot}00235T^2 + 68{\cdot}6T$. F. R. Bichowsky recommended the following process:

A conc. soln. of calcium chloride is added to a cold conc. soln. of sodium thiosulphate. Sodium chloride separates out. The crystals of calcium thiosulphate can then be fractionally crystallized by adding alcohol, redissolving the precipitate in water and reprecipitating with alcohol. This method works well with small quantities if a trace of alcohol is no objection. For large quantities, the best method is to dissolve 510 grms. of crystallized sodium thiosulphate in 465 grms. of water, then add, with constant stirring, 350 grms. of finely crystallized calcium chloride dihydrate. The temp. of the soln. should not rise above 60° during this process. The soln. is allowed to stand overnight, and the clear liquid is decanted through a larger filter, and cooled to 0° or −10° and allowed to crystallize. Prepared in this way, the crystals contain only a small amount of sodium chloride as an impurity, from which they can be freed by recrystallization. The solid salt dehydrates rapidly at room temp., also decomposing into sulphur and sulphite at the same time. In contact with its sat. soln. it is stable for several weeks at 25°. At 0°, it is apparently indefinitely stable. The $2M$-soln. is stable up to about 35°, and is the most convenient form in which to keep the salt.

The transparent, six-sided crystals were found by V. von Zepharovich to belong to the triclinic system, and to have the axial ratios $a:b:c = 0{\cdot}7828:1:1{\cdot}5170$,



FIGS. 125 and 126.—Equilibria in the System: $CaS_2O_3 + 2NaNO_3 \rightleftharpoons Na_2S_2O_3 + Ca(NO_3)_2$, at 9° and 25°.

and $\alpha = 72° 30'$, $\beta = 98° 34'$, and $\gamma = 92° 45\frac{3}{4}'$. The (100)-cleavage is perfect. W. T. Astbury found that the X-radiogram corresponded with a space lattice having two mols of $CaS_2O_3.6H_2O$ per unit cell. F. W. Clarke found the sp. gr. at 13·5° to be 1·8175; and at 16°, 1·8728. J. F. W. Herschel found that the crystals effloresce in vacuo over sulphuric acid at ordinary temp., and in air over 40°. E. Kopp found that the crystals cannot be kept in a closed vessel without decomposing into sulphur and calcium sulphite; and J. F. W. Herschel observed a similar result with a conc., aq. soln. over 60°. C. F. Rammelsberg said that when the salt is heated out of contact with air, water and sulphur are given off, while a mixture of calcium sulphide, sulphite, and sulphate remains; and, according to A. Forster, this mixture is phosphorescent. The heat of the reaction $CaS_2O_3(0{\cdot}2127 \text{ mol per litre}) = CaSO_3.2H_2O + S_{\text{rhombic}} - 6300$ cals.; the heat of dilution is $Q = (n - 22{\cdot}5)/(0{\cdot}107 + 0{\cdot}00168n)$ cals., where n is the number of mols of water in the final soln. per mol of thiosulphate. For soln. with M-mols per litre:

M . .	1·750	1·3234	0·888	0·447	0·213
Sp. ht. . .	7·004	0·769	0·840	0·918	0·954

O. Stelling studied the absorption spectrum of X-rays. C. Pape gave 2·09° for the rotary polarization of the crystals. J. F. W. Herschel found that water dissolves its own weight of the salt at 3°; and a part of the calcium is precipitated from the aq. soln. by potassium carbonate; and the remainder is precipitated when the soln. is heated. F. R. Bichowsky gave 2·28 grms. per litre for the solubility of the hexahydrate at 25°. R. Kremann and H. Rodemund studied the equilibrium in the reversible reaction $CaS_2O_3+Na_2CO_3 \rightleftharpoons Na_2S_2O_3+CaCO_3$; in $CaS_2O_3 + Na_2SO_4 \rightleftharpoons Na_2S_2O_3 + CaSO_4$; and in $CaS_2O_3 + 2NaNO_3 = Ca(NO_3)_2 + Na_2S_2O_3$. The results with the last-named reaction, at 9° and 25°, are summarized in Figs. 125 and 126.

The point A refers to $NaNO_3$; B, to $Ca(NO_3)_2.4H_2O$; C, to $CaS_2O_3.6H_2O$; D, to $Na_2S_2O_3.5H_2O$; E, a sat. soln. of both $NaNO_3$ and $Ca(NO_3)_2.4H_2O$; H, a sat. soln. of both $CaNO_3.4H_2O$ and $Ca_2S_2O_3.6H_2O$; F, a sat. soln. of both $NaNO_3$ and $Na_2S_2O_3.5H_2O$; and G, to a sat. soln. of both $Na_2S_2O_3.5H_2O$ and $CaS_2O_3.6H_2O$. The curves AE, and AF refer to soln. sat. with $NaNO_3$ with increasing proportions respectively of $Ca(NO_3)_2$ and $Na_2S_2O_3$; BE, and BH, to sat. soln. of $Ca(NO_3)_2.4H_2O$ with increasing proportions respectively of $NaNO_3$ and CaS_2O_3; CH, and CG, to sat. soln. of $CaS_2O_3.6H_2O$ with increasing proportions respectively of $Ca(NO_3)_2$ and $Na_2S_2O_3$; and DG, and DF, to sat. soln. of $Na_2S_2O_3.5H_2O$ with increasing proportions of CaS_2O_3 and $NaNO_3$ respectively. The area $EBHP$ refers to the sat. soln. $Ca(NO_3)_2.4H_2O$; EPR_3R_2FA, to $NaNO_3$; FR_2R_1GD, to $Na_2S_2O_3.5H_2O$; $GCHPR_3R_1$, to $CaS_2O_3.6H_2O$; and $R_3R_2R_1$, to the triple salt $Na_3Ca(S_2O_3)_2(NO_3).11H_2O$.

J. F. W. Herschel, and F. Kessler obtained **strontium thiosulphate,** SrS_2O_3, as in the case of the calcium salt. The liquid is filtered from any carbonate or sulphate, and on evaporation, J. L. Gay Lussac obtained rhombohedral crystals; and by adding alcohol, T. von Grotthus obtained a crystalline mass. F. Kessler mixed a hot, conc. soln. of strontium chloride or nitrate with the calculated quantity of sodium thiosulphate, and obtained the strontium thiosulphate by evaporation or by adding alcohol—methyl alcohol for preference, added S. Kern. Two hydrates have been reported. F. Kessler said that prismatic crystals of the *monohydrate* are produced when the aq. soln. is evaporated above 50°; and the *pentahydrate* is obtained below that temp. and, according to R. Portillo, by crystallization from alcohol. The analyses of C. F. Rammelsberg, J. C. G. de Marignac, and E. A. Letts show that the crystals are pentahydrated and not hexahydrated as supposed by F. W. Clarke. A. Fock and K. Klüss found the monohydrate furnishes monoclinic crystals with the axial ratios $a : b : c = 1{\cdot}2946 : 1 : 2{\cdot}584$, and $\beta = 107° 32'$. Twinning occurs about the (100)-plane. J. C. G. de Marignac, and C. F. Rammelsberg found that the monoclinic crystals of the pentahydrate have the axial ratios $a : b : c = 1{\cdot}2946 : 1 : 2{\cdot}5848$, and $\beta = 107° 32'$. Twinning occurs about the (001)-plane, and the (001)-cleavage is perfect. C. Pape gave 1·64° for the rotary polarization of the crystals. F. W. Clarke gave 2·1566 to 2·1991 at 17° for the sp. gr. of the crystals of the pentahydrate. R. Portillo gave 2·202 for the sp. gr. of the pentahydrate at 25°/4°, and 2·916 for that of the monohydrate at 25°/4°. The mol. vol. of the contained water is 14·22. J. L. Gay Lussac said that the crystals taste insipid at first and afterwards appear sulphureous; they are neutral to vegetable colours; and are permanent in air. On the other hand, J. C. G. de Marignac found that the crystals slowly effloresce in air, and crumble to dust. According to J. L. Gay Lussac, the water of crystallization is expelled between 50° and 60°, and at higher temp., the salt forms strontium sulphide and sulphate, with the separation of sulphur. C. F. Rammelsberg, however, found that the salt does not part with all its water at 60°, and that it even retains 6 per cent. at 180°. At a higher temp., it is resolved into a mixture of strontium sulphide, sulphite, and sulphate, with the loss of water, sulphur, and sulphide dioxide—the residue, according to A. Forster, is phosphorescent. J. L. Gay Lussac said that 100 parts of cold water dissolve 16·67 parts of salt; W. Autenrieth and A. Windaus, 27 parts of salt at room temp.; and J. F. W. Herschel, 25 parts of salt at 4°. R. Portillo found that the percentage solubility of the pentahydrate at 0°, 12·8°, 27·5°, and 40° is 8·78, 13·82, 21·10, and

26·80 ; the mol. heat of soln. is —7·34 cals. ; and for the monohydrate, 2·38 cals. ; the heat of hydration of the pentahydrate, starting from the monohydrate, is 9·7 cals. J. L. Gay Lussac said that nitric acid converts the salt into the sulphate.

H. Rose obtained **barium thiosulphate,** BaS_2O_3, by crystallization from a soln. of barium sulphide exposed to air ; E. A. Letts, and A. Forster by cooling a hot soln. of barium chloride or acetate and sodium thiosulphate—the addition of alcohol precipitates more barium thiosulphate from the soln. ; and T. Curtius and F. Henkel, by treating Wackenroder's liquid with barium carbonate, and adding alcohol to the filtrate which is then cooled for crystallization. A. Sobrero and F. Selmi found that it is precipitated by alcohol from its aq. soln. According to B. C. Brodie, when barium dioxide is triturated with a mixture of carbon disulphide and water, a yellow liquid is obtained which when allowed to stand slowly deposits barium carbonate—rapidly if boiled—and, if an excess of the dioxide is present, the liquid contains barium thiosulphate. The rhombic needles or plates of monohydrated barium thiosulphate were found by H. Bäckström to have the axial ratios $a : b : c = 0·7304 : 1 : 0·7248$; the (010)-cleavage is perfect, and the (001)-cleavage distinct. F. W. Clarke gave 3·4461 for the sp. gr. at 16°, and 3·4486 at 18°. H. Rose, E. A. Letts, and T. Curtius found that crystals of the *monohydrate* are obtained at ordinary temp., but, when dried at 100°, or after standing over sulphuric acid, E. A. Letts, and T. Curtius found that the anhydrous salt is obtained ; while C. F. Rammelsberg, and C. Pape said that the water is expelled only when heated over 170°. H. Rose said that when the crystals are heated in a closed vessel, water, hydrogen sulphide, and sulphur are given off, while a mixture of barium sulphide and sulphate remains ; and C. F. Rammelsberg observed that the salt dried at 170° loses at a red-heat water and sulphur, but not hydrogen sulphide or sulphur dioxide, and leaves a sintered mixture of barium sulphide, sulphite, and sulphate which A. Forster found to be luminous. H. Rose observed that the salt is sparingly soluble in water ; and W. Autenrieth and A. Windaus, that at room temp., 100 parts of water dissolve 0·208 part of salt. According to A. Naumann, it is insoluble in acetone ; and also insoluble in alcohol. W. Spring found that sulphur monochloride converts the thiosulphate into pentathionate ; and G. Chancel and E. Diacon, that cupric sulphate forms copper tetrathionate which rapidly decomposes. V. J. Sihvonen found maxima in the ultra-red reflection spectrum at 9·3μ, 10·4μ, 15·0μ, and 18·2μ.

K. Diehl found that a sat. soln. of sodium thiosulphate dissolved some calcium sulphate, and alcohol precipitates an oily liquid which later crystallizes, forming **sodium calcium thiosulphate.** A. Fock and K. Klüss prepared **barium dichlorothiosulphate,** $BaCl_2.BaS_2O_3.2H_2O$, from a soln. containing the component salts. R. Kremann and H. Rodemund prepared the triple salt : **sodium calcium nitratodithiosulphate,** $NaNO_3.Na_2S_2O_3.CaS_2O_3.11H_2O$, from a mixture of the component salts in the regions of stability indicated in Figs. 125 and 126. The solubility, *S* per cent. of anhydrous triple salt, is :

	1°	9°	15°	20°	25°	27°	28°	30°	33°
S . .	42·14	43·61	46·29	50·40	56·28	58·86	60·99	63·30	58·43
	$CaNa_3(NO_3)(S_2O_3)_2$							Decomposition	

The results are plotted in Fig. 127. The region of decomposition refers to the reversible reaction : $Na_3Ca(NO_3)(S_2O_3)_2.11H_2O \rightleftharpoons NaNO_3 + Na_2S_2O_3.5H_2O + CaS_2O_3.6H_2O$. A. Fock and K. Klüss, and G. Wyrouboff obtained **potassium calcium thiosulphate,** $3K_2S_2O_3.CaS_2O_3.5H_2O$, by evaporating a mixed soln. of the component salts. The monoclinic prisms have the axial ratios $a : b : c = 1·7010 : 1 : 0·8931$, and $\beta = 99° 58'$. A. Fock and K. Klüss also made **potassium strontium thiosulphate,** $K_2S_2O_3.SrS_2O_3.5H_2O$. J. F. W. Herschel, and A. Rosenheim and S. Steinhäuser made **cuprous calcium thiosulphate**—possibly $2CaS_2O_3.Cu_2S_2O_3.nH_2O$—by mixing soln. of calcium thiosulphate and copper sulphate, or by digesting the soln. of calcium thiosulphate with copper carbonate. When the soln. is mixed with an excess of ammonia, it becomes blue on exposure to air. C. F. Rammelsberg, and J. B. Cohen obtained a complex salt by treating potassium cuprous thiosulphate soln. with barium chloride; A. Rosenheim and A. Steinhäuser obtained white, amorphous *tetrahydrated* **cuprous barium trithiosulphate,** $2BaS_2O_3.Cu_2S_2O_3.4H_2O$, from a cold sat. soln. of the ammonium complex salt and barium chloride, and drying the product in air; if the sodium complex salt is used, G. Vortmann found that the *heptahydrate* is formed as a white precipitate sparingly soluble in water, but soluble in hydrochloric acid. J. F. W. Herschel made **silver strontium dithiosulphate,** $SrS_2O_3.Ag_2S_2O_5.2H_2O$, by the action of a soln. of strontium thiosulphate on silver chloride; and K. Barth, by adding strontium chloride to a soln. of sodium silver trithiosulphate, when iridescent crystals appear in a short time. He also obtained **silver barium trithiosulphate,** $2BaS_2O_3.Ag_2S_2O_3$, in an analogous way. M. J. Fordos and A. Gélis prepared **gold barium thiosulphate,** as a precipitate, by mixing aq. soln. of sodium gold thiosulphate and barium chloride, and adding alcohol. The product is slightly soluble in water, and insoluble in alcohol.

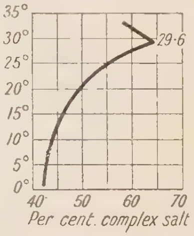


FIG. 127.—Solubility of $Na_3Ca(S_2O_3)_2(NO_3)$.

F. J. Faktor [8] prepared **beryllium thiosulphate,** $BeS_2O_3.11H_2O$, by crystallization from the soln. obtained by mixing sodium thiosulphate and beryllium sulphate —*vide infra*, aluminium thiosulphate. J. F. W. Herschel, and C. F. Rammelsberg obtained **magnesium thiosulphate,** $MgS_2O_3.6H_2O$, by boiling an aq. soln. of magnesium sulphate with flowers of sulphur, but the product is difficult to free from sulphide and sulphate. E. A. Letts obtained it by double decomposition with magnesium sulphate and strontium thiosulphate—barium thiosulphate can be used. The filtrate is evaporated over conc. sulphuric acid when rhombic prisms are obtained. A. Fock and K. Klüss found the axial ratios of the rhombic bipyramids to be $a:b:c=0·7674:1:0·7294$, and F. W. Clarke gave 1·818 for the sp. gr. F. Kohlrausch and L. Holborn represented for the eq. electrical conductivity, λ, of soln. with an eq. of the salt in v litres:

v . .	32	64	128	256	512	1024
λ . .	94·1	105·1	113·9	122·2	128·8	135·2

P. Walden made observations on this subject. C. F. Rammelsberg said that the crystals are stable in air; they lose about half their water of crystallization; and E. A. Letts said that about 3 mols. are lost at 100°. C. F. Rammelsberg found that when strongly heated, the salt gives off water, sulphur, and sulphur dioxide, the residue sinters, forming a mixture of magnesium oxide, sulphite, and sulphate. The salt is freely soluble in water, and alcohol precipitates an oily liquid from the conc. aq. soln. F. Kessler prepared **ammonium magnesium thiosulphate,** $(NH_4)_2S_2O_3.MgS_2O_3.6H_2O$, by double decomposition with ammonium magnesium sulphate and strontium thiosulphate, and cooling the conc. soln. below 0°; a conc. soln. of the component salts also yields, at 35°, prismatic, non-hygroscopic crystals which lose no water in vacuo, or over sulphuric acid. The monoclinic prisms have the axial ratios $a:b:c=0·6422:1:0·9238$, and $\beta=105° 34'$. The (101)-cleavage is perfect. F. Kessler, C. F. Rammelsberg, and A. Fock and K. Klüss prepared crystals of **potassium magnesium thiosulphate,** $K_2S_2O_3.MgS_2O_3.6H_2O$, in monoclinic tabular or prismatic crystals from a soln. of the component salts. The axial ratios given by A. Fock and K. Klüss are $a:b:c=2·0001:1:1·0474$, and $\beta=107° 31'$. J. Meyer and H. Eggeling obtained **rubidium magnesium thiosulphate,** $Rb_2S_2O_3.MgS_2O_3.6H_2O$, from a soln. of the component salts. The transparent columnar crystals are freely soluble in water; similarly with **cæsium magnesium thiosulphate,** $Cs_2S_2O_3.MgS_2O_3.6H_2O$.

W. Hampe [9] reported the presence of some hydrated **zinc thiosulphate,** $ZnS_2O_3.nH_2O$, in the flue dust of a zinc furnace. A. F. de Fourcroy and L. N. Vauquelin obtained crystals of zinc sulphite mixed with those of zinc thiosulphate when sulphurous acid acts on zinc: $2Zn+3H_2SO_3=ZnSO_3+ZnS_2O_3+3H_2O$; F. Wöhler said that a mixture of zinc sulphide and sulphate are formed by the action of sulphurous acid on zinc; E. Mitscherlich said that the products of the action are zinc sulphite which crystallize out, and zinc thiosulphate which remains in soln., and, added J. J. Berzelius, and C. J. Koene, if the acid becomes very hot hydrogen sulphide is formed and some of the zinc in soln. is reprecipitated. H. Risler-Beunat said that some pentathionate is also formed during the reaction. According to W. E. Henderson and H. B. Weiser, when freshly precipitated iron, zinc, or manganese sulphide is suspended in water and a current of sulphur dioxide introduced, the sulphide rapidly dissolves, and the sulphite of the metal is gradually deposited, the reaction being represented by the equation: $MS+H_2SO_3=MSO_3+H_2S$. On continuing to pass sulphur dioxide into the mixture, the sulphite dissolves to form the hydrosulphite. If the soln. of the hydrosulphite is boiled, the sulphite is re-deposited. The soln. now contains thiosulphate, which is produced by the action of sulphur, formed by the interaction of sulphurous acid and hydrogen sulphide, on the hydrogen sulphite, thus: $M(HSO_3)_2+S=MS_2O_3+H_2O+SO_2$. These and other experiments show that the reaction between sulphurous acid and the sulphides of zinc, iron, and manganese is a double decomposition of the usual type, and that, in so far as the conditions lead to the oxidation of the liberated hydrogen sulphide by the sulphurous acid, a certain amount of thiosulphate is produced by a secondary reaction.

J. J. Berzelius obtained zinc thiosulphate by the action of sulphur on a soln. of zinc sulphite confined in a closed vessel; C. F. Rammelsberg, by passing sulphur dioxide through water with freshly precipitated zinc sulphide in suspension—dissolution takes place with difficulty, and is attended by the deposition of sulphur; C. F. Rammelsberg filtered the soln. remaining after zinc sulphate has reacted with barium thiosulphate—A. Rosenheim and I. Davidsohn added the powdered barium salt to the soln. of zinc sulphate, and agitated the liquid for some days at the ordinary temp. The salt is so easily decomposed that it has not been obtained in the solid state; and M. J. Fordos and A. Gélis observed that if the colourless and odourless soln., which is not precipitated by alcohol, be evaporated at ordinary temp. in air or in vacuo, zinc sulphide is deposited when the soln. has become concentrated, and zinc trithionate remains in soln., while C. F. Rammelsberg said that sulphur is precipitated, and zinc sulphate remains in soln. According to C. J. Koene, if ether be added to the aq. soln., an oil is precipitated, and this dries in vacuo to a gummy mass. C. F. Rammelsberg added that if the aq. soln. of zinc thiosulphate be sat. with ammonia, and absolute alcohol added, white needles of **zinc diamminothiosulphate,** $ZnS_2O_3.2NH_3$, are formed. This salt is hydrolyzed by water. F. Ephraim and E. Bolle obtained **zinc triamminothiosulphate,** $ZnS_2O_6.3NH_3.nH_2O$, by saturating a soln. of zinc thiosulphate with ammonia; and **zinc pentamminothiosulphate,** $ZnS_2O_3.5NH_3.nH_2O$, by treating the dry salt with ammonia. A. Rosenheim and I. Davidsohn prepared **ammonium zinc thiosulphate,** $(NH_4)_2Zn(S_2O_3)_2.H_2O$, in white, prismatic crystals, from aq. soln., and likewise **potassium zinc thiosulphate,** $K_2Zn(S_2O_3)_2.H_2O$. Both salts are very soluble in aq. soln., and give the ordinary reactions for zinc.

G. Vortmann and C. Padberg prepared **cadmium thiosulphate,** $CdS_2O_3.2H_2O$, by triturating a mixture of stoichiometrical proportions of cadmium sulphate and barium thiosulphate with a little water, and mixing the filtrate with alcohol. A. Fock and K. Klüss used strontium thiosulphate, and used a mixture of alcohol and ether as the precipitant. The yellowish-white, monoclinic crystals have the (010)-cleavage nearly complete. The crystals slowly decomposed when kept in closed vessels—more rapidly when heated—forming cadmium sulphide and sulphate, and sulphur dioxide. A. Fock and K. Klüss obtained monoclinic prisms of **ammonium cadmium dithiosulphate,** $(NH_4)_2S_2O_3.CdS_2O_3$, by adding alcohol to a soln. of 2 mols of cadmium acetate and 3 mols of ammonium thiosulphate. The axial ratios are

$a:b:c=0{\cdot}8216:1:1{\cdot}5560$, and $\beta=97°\ 45'$. The basal cleavage is complete. By keeping the molar ratio of the constituents 1 : 4 respectively, *monohydrated* **ammonium cadmium tetrathiosulphate,** $3(NH_4)_2S_2O_3.CdS_2O_3.H_2O$, is formed in rhombic crystals with the axial ratios $a:b:c=0{\cdot}4317:1:0{\cdot}4187$; and with the proportion 1 : 4 to 7, the *trihydrate* is formed in monoclinic plates with the axial ratios $a:b:c=0{\cdot}9760:1:1{\cdot}0026$, and $\beta=96°\ 15'$. By mixing an excess of sodium thiosulphate with cadmium acetate, *trihydrated* **trisodium cadmium tetrathiosulphate,** $3Na_2S_2O_3.CdS_2O_3.3H_2O$, is formed in yellow, deliquescent, triclinic crystals; G. Vortmann and C. Padberg obtained yellow plates of the enneahydrate by adding alcohol to a soln. of cadmium nitrate and an excess of sodium thiosulphate, and rubbing up the oil with alcohol. The crystals lose 4 mols. of water over conc. sulphuric acid. A. Fock and K. Klüss prepared the *hexahydrate* by adding alcohol to a soln. of cadmium acetate and an excess of sodium thiosulphate. P. Jochum said that at least 3 parts of a cold sat. soln. of sodium thiosulphate are needed for 2 parts of a similar soln. of cadmium acetate. The yellow, monoclinic plates have the axial ratios $a:b:c=1{\cdot}136:1:0{\cdot}3492$, and $\beta=103°\ 35'$. The (010)-cleavage is complete. The crystals lose all their water in vacuo over sulphuric acid; they decompose at 90°, and are very soluble in water; the salt is hydrolyzed by boiling the aq. soln. G. Vortmann and C. Padberg added alcohol to soln. of equal parts of cadmium nitrate and sodium thiosulphate, and obtained yellowish-white needles of **sodium dicadmium trithiosulphate,** $Na_2S_2O_3.2CdS_2O_3.7H_2O$; and with a soln. of these salts in molar proportions, **sodium tricadmium tetrathiosulphate,** $Na_2S_2O_3.3CdS_2O_3.9H_2O$. A. Fock and K. Klüss could not prepare this salt. H. Euler found that although **sodium cadmium dithiosulphate,** $Na_2S_2O_3.CdS_2O_3$, has not been obtained in the solid state, it is probably present in soln., and the equilibrium constant K for $[Cd][S_2O_3]^2[Na_2S_2O_3]=K[CdNa_2(S_2O_3)_4]$ is $3{\cdot}5\times10^{-8}$ to 5×10^{-8}.

A. Fock and K. Klüss prepared **potassium cadmium octothiosulphate,** $5K_2S_2O_3.3CdS_2O_3$, by mixing equal vols. of conc. soln. of cadmium acetate and potassium thiosulphate. The salt cannot be recrystallized from water without decomposition. The monoclinic crystals have the axial ratios $a:b:c=1{\cdot}3203:1:0{\cdot}9565$, and $\beta=92°\ 26'$. They also made **potassium cadmium tetrathiosulphate,** $3K_2S_2O_3.CdS_2O_3.2H_2O$, by adding alcohol to a soln. of 6 mols of potassium thiosulphate and a mol of cadmium acetate. The colourless, monoclinic prisms have the axial ratios $a:b:c=1{\cdot}5103:1:0{\cdot}9631$, and $\beta=100°\ 39'$. The salt can be recrystallized from water without decomposition; over sulphuric acid, in vacuo, it loses a mol. of water. By treating a mixed soln. of calcium thiosulphate and cadmium acetate with alcohol, a gummy mass of **calcium cadmium thiosulphate** is formed; but yellow plates of **strontium cadmium tetrathiosulphate,** $3SrS_2O_3.CdS_2O_3.10H_2O$, can be obtained under similar conditions. They quickly lose 5 mols. of water over sulphuric acid, and 2 mols. more are given off slowly. An aq. soln. of a mol. of cadmium sulphate and 2 mols. of barium thiosulphate, yields triclinic crystals of **barium cadmium trithiosulphate,** $2BaS_2O_3.CdS_2O_3.8H_2O$. They have the axial ratios $a:b:c=0{\cdot}9871:1:0{\cdot}8595$, and $\alpha=80°\ 15'$, $\beta=91°\ 37'$, and $\gamma=57°\ 50'$. If the filtrate obtained in the preparation of this salt be treated with alcohol, triclinic plates of **barium cadmium tetrathiosulphate,** $3BaS_2O_3.CdS_2O_3.8H_2O$, are formed having the axial ratios $a:b:c=0{\cdot}6997:1:0{\cdot}6441$, and $\alpha=94°\ 18'$, $\beta=91°\ 18'$, and $\gamma=79°\ 11'$.

Our knowledge of the mercury thiosulphates is in an unsatisfactory state—*vide supra,* the chemical properties of the thiosulphates. F. J. Faktor[10] found that aq. soln. of mercurous or mercuric salts are precipitated at the b.p. by sodium thiosulphate, with formation of mercuric sulphide. One mol of sodium thiosulphate corresponds with a mol of mercuric chloride. R. Behrend made some electrometric observations on soln. supposed to contain **mercurous thiosulphate,** $Hg_2S_2O_3$, but the salt itself has not been isolated. C. F. Rammelsberg was unable to isolate **mercuric thiosulphate,** HgS_2O_3, and the salt is known only when combined with other thiosulphates as a complex salt. H. Dreser said that in these salts, the mercury is present as a complex radicle, forming *hydromercurithiosulphuric acid*, $H_2Hg(S_2O_3)_2$. G. S. Kirchhoff prepared what he regarded as a complex salt with ammonium thiosulphate; and C. F. Rammelsberg found that mercuric oxide dissolves in a soln. of ammonium thiosulphate with the evolution of heat, and the addition of alcohol furnishes **ammonium mercuric pentathiosulphate,** $4(NH_4)_2S_2O_3.HgS_2O_3.2H_2O$. The colourless crystals readily decompose; they become grey in light; and the aq. soln. precipitates black mercuric sulphide when boiled. H. Hirzel could only obtain an impure salt by C. F. Rammelsberg's process, and H. Eggeling said that the product is a solid soln. of the component thiosulphates. J. Schnauss mixed moist mercurous chloride with a soln. of sodium thiosulphate, and found that alcohol added to the conc. and filtered soln. gave oily drops of **sodium mercurous thiosulphate,** which ultimately form a mass of crystals. The salt acquires a film of orange-yellow mercuric sulphide, which soon blackens in light. The salt is very deliquescent, and very soluble in water. The aq. soln. when boiled deposits mercuric sulphide. According to J. F. W. Herschel, mercuric oxide dissolves in a soln. of sodium thiosulphate, and when the soln. is evaporated it becomes turbid and deposits mercuric sulphide; and, according to C. F. Rammelsberg, alcohol precipitates from the soln. an oily liquid which on standing slowly deposits mercuric sulphide. The solid was not isolated, but the oily liquid corresponds with **sodium mercurous thiosulphate,** $Na_2S_2O_3.Hg_2S_2O_3.nH_2O$. When boiled with water, W. Spring said that mercuric sulphide and sodium trithionate are formed. G. S. Kirchhoff dissolved 2 parts of mercuric oxide in a soln. of 5 parts of potassium thiosulphate in 24 parts of hot water; when the filtered soln. is cooled, crystals of **potassium mercurous octothiosulphate,** $5K_2S_2O_3.3Hg_2S_2O_3$, separate out. C. F. Rammelsberg added that in this mode of preparation, the soln. should not be boiled, or mercuric sulphide will be precipitated, and if mercurous oxide is used, metallic mercury remains undissolved. A. Fock and K. Klüss obtained the salt by evaporating the soln. on a water-bath; and J. M. Eder and G. Ulm precipitated the salt by adding alcohol to a soln. of mercuric iodide in a soln. of potassium thiosulphate. The colourless plates were found by A. Fock and K. Klüss to be monoclinic with the axial ratios $a : b : c = 0{\cdot}332 : 1 : 0{\cdot}318$, and $\beta = 91° 51'$. H. Eggeling supposed the crystals are a solid soln. of the component salts. G. S. Kirchhoff said that the crystals have a bitter taste which afterwards appears metallic; they do not redden turmeric, and they become grey when dried. They do not effloresce in air, and when heated alone they form sulphur and its dioxide, mercury and its sulphide, and potassium sulphate; and when distilled with water they furnish sulphurous acid, mercuric sulphide, sulphur, and potassium sulphate. C. F. Rammelsberg said that the crystals turn black when exposed to light; but A. Fock and K. Klüss observed no blackening under these conditions. According to G. S. Kirchhoff, 100 parts of water dissolve 10 parts of the salt at 15°, and boiling water dissolves 50 parts of salt; alcohol precipitates it from its aq. soln. Hydrochloric, sulphuric, or nitric acid makes the aq. soln. turbid in a few minutes, mercuric sulphide is precipitated, and sulphur dioxide evolved—C. F. Rammelsberg said that some sulphur is formed as well. G. S. Kirchhoff observed no action with sulphurous or acetic acid, or with alkali-lye; baryta-water or lime-water slowly forms a greyish-yellow precipitate; mercurous nitrate a black or grey precipitate; and bismuth, lead, iron, and copper decompose the salt. C. F. Rammelsberg added that lead salts give a white precipitate; and silver salts a precipitate containing mercury. A. Fock and K. Klüss also reported colourless monoclinic prisms of **potassium mercuric tetrathiosulphate,** $3K_2S_2O_3.HgS_2O_3.3H_2O$, to be formed by using an excess of potassium thiosulphate as in the preparation of the preceding salt. The axial ratios are $a : b : c = 1{\cdot}4843 : 1 : 0{\cdot}9463$, and $\beta = 101° 5'$. By using a still larger excess of potassium thiosulphate, they obtained triclinic prisms of **potassium mercurous hexathiosulphate,** $5K_2S_2O_3.Hg_2S_2O_3.H_2O$. C. F. Rammelsberg prepared what he regarded as **cuprous mercurous octothiosulphate,** $5Cu_2S_2O_3.3Hg_2S_2O_3$, as a reddish-brown precipitate when a soln. of potassium mercuric thiosulphate is treated with cupric oxide. He could not obtain a crystalline barium mercuric thiosulphate from a soln. of mercuric oxide in one of barium thiosulphate; and similarly also with **strontium mercuric thiosulphate;** and with **calcium mercuric thiosulphate.**

J. M. Eder and G. Ulm found that mercuric iodide dissolves in an aq. soln. of sodium thiosulphate, forming a clear liquid containing $HgI_2 : Na_2S_2O_3$ in the molar proportion 1 : 2. It is assumed that the soln. contains the complex **sodium mercuric diiododithiosulphate,** $HgI_2.2Na_2S_2O_3$. On leaving a cold sat. soln. to evaporate in vacuo, over sulphuric acid, sulphur dioxide is evolved, and a yellow precipitate of mercurous iodide is formed, which quickly turns green, and subsequently becomes mixed with sulphur and mercuric sulphide. On evaporating it to dryness, mercuric sulphide and sodium iodide are formed. Alcohol precipitates $HgS_2O_3.2Na_2S_2O_3$; but the soln. is not clouded by ammonia, ammonium carbonate, and potassium hydroxide, ferrocyanide, or ferricyanide. The soln. decomposes, with or without contact with air, in a few weeks at ordinary temp., or in a few hours when heated. The soln. acts on finely-divided silver, turning it black.

G. Vortmann[11] found that when aluminium chloride is treated with sodium thiosulphate, the reaction can be symbolized: $Al_2Cl_6+3Na_2S_2O_3+3H_2O=Al_2(OH)_6+6NaCl+3S+3SO_2$. Tetrathionic acid is formed in quantity corresponding with that obtainable from about 4 per cent. of the thiosulphate employed, and at the commencement of the reaction a small quantity of hydrogen sulphide escapes, but no trace of sulphuric acid could be detected. The addition of potassium iodide at the commencement of the experiment brings about the formation of sulphuric acid in this case also. An **aluminium thiosulphate** has not been prepared. If a soln. of aluminium chloride, nearly neutralized with sodium carbonate, be treated with an excess of sodium thiosulphate, and boiled until the smell of sulphur dioxide is no longer perceptible, aluminium hydroxide will be precipitated: $2AlCl_3+3Na_2S_2O_3+3H_2O=2Al(OH)_3+6NaCl+3S+3SO_2$. If the corresponding salts of zirconium, titanium, and thorium be present, they too will be precipitated as hydroxides, but not so with salts of iron, beryllium, cerium, lanthanum, didymium, etc. The reaction was utilized by F. Chancel, etc., in analytical work.

W. Crookes,[12] P. Jochum, and M. Hebberling showed that sodium thiosulphate precipitates **thallous thiosulphate,** $Tl_2S_2O_3$, from not too dil. soln. of a thallous salt. H. Euler said that the crystalline salt is sparingly soluble in cold water, and M. Hebberling, that it is freely soluble in hot water, and it separates out from the hot soln. on cooling. H. Euler referred that greater solubility of the salt in soln. of sodium thiosulphate to the formation of a complex salt. This soln., or a soln. of thallous chloride in a boiling soln. of sodium thiosulphate, furnishes long needles of **sodium thallous pentathiosulphate,** $3Na_2S_2O_3.2Tl_2S_2O_3.8$ or $10H_2O$; and the salt can be recrystallized from water. The salt was so prepared by G. Werther, H. Euler, and P. Jochum. It loses all its water at 120°; and when heated out of contact with air, it forms thallous and sodium sulphides and sodium sulphate. G. Vortmann and C. Padberg also obtained needle-like crystals of **sodium thallous trithiosulphate,** $2Na_2S_2O_3.Tl_2S_2O_3.8H_2O$, by adding alcohol to a soln. of a thallous salt in an excess of a soln. of sodium thiosulphate. G. Canneri prepared **thallous cupric thiosulphate,** $Tl_4Cu(S_2O_3)_3$, as a straw-yellow, microcrystalline powder.

R. J. Meyer[13] obtained **scandium hydroxythiosulphate,** $Sc(OH)S_2O_3$, as a precipitate by adding sodium thiosulphate to a soln. of scandium nitrate or chloride. The **rare earth thiosulphates** have not been examined very closely. P. T. Cleve obtained samarium thiosulphate by the action of a salt of that earth and a soln., of sodium thiosulphate. For the general behaviour of the rare earths to this soln. *vide supra.* G. Canneri and L. Fernandes prepared a series of cuprothiosulphates of the rare earths by mixing soln. of copper sulphate and a soluble rare earth salt, each previously sat. with sulphur dioxide. They thus prepared **cerium cuprous dithiosulphate,** $CeCu(S_2O_3)_2.8H_2O$; **lanthanum cuprous dithiosulphate,**

$LaCu(S_2O_3)_2.8H_2O$; **praseodymium cuprous dithiosulphate,** $PrCu(S_2O_3)_2.8H_2O$; **neodymium cuprous dithiosulphate,** $NdCu(S_2O_3)_2.8H_2O$. The thiosulphates of titanium, zirconium, and thorium have not been closely examined. No **titanium thiosulphate** has been prepared. M. Weibull added that in the case of zirconium salts, **zirconium thiosulphate** was precipitated in the cold, and a basic salt when heated. G. Canneri and L. Fernandes made **zirconium cuprous trithiosulphate,** $ZrCu(S_2O_3)_3.30H_2O$, by the method used for the rare-earth salts. **Thorium thiosulphate** has not been prepared, but G. Canneri and L. Fernandes obtained **thorium cuprous dithiosulphate,** $ThCu(S_2O_3)_2.8H_2O$, as in the case of the rare-earth salts.

According to A. F. de Fourcroy and L. N. Vauquelin,[14] sulphurous acid forms **stannous thiosulphate** when it reacts with tin ; but, according to M. J. Fordos and A. Gélis, only a small yield is so obtained. According to G. Vortmann, when a feebly acidic soln. of stannous chloride is boiled with sodium thiosulphate, a yellow precipitate of stannous hydroxide is formed, and sulphuric and pentathionic acids pass into soln., similar results are obtained with stannic chloride. A. L. Orlowsky found that the tin is completely precipitated from hot hydrochloric acid soln. of stannous chloride, but not completely from strongly acid soln. G. Tocco and N. Jacob obtained tin sulphides and thiosulphate by the alternating current electrolysis of a soln. of sodium thiosulphate with tin electrodes.

J. F. W. Herschel precipitated **lead thiosulphate,** PbS_2O_3, from a soln. of lead nitrate by adding a soln. of calcium thiosulphate, and J. Meyer and H. Eggeling, and W. H. Perkins and A. T. King used a soln. of sodium thiosulphate. The precipitate was washed by decantation, then on a filter, and dried in vacuo. If the soln. be boiling, H. Vohl found that the precipitate is white, but with a prolonged boiling, F. J. Faktor found that it acquires a grey colour. In place of lead nitrate, F. Kessler, W. H. Perkins and A. T. King, E. A. Letts, J. Fogh, and P. Jochum employed lead acetate, and W. H. Perkins and A. T. King, a hot soln. of lead formate or lead trichloroacetate. A. Chwala and H. Colle obtained lead thiosulphate by the action of an excess of sodium thiosulphate on lead dioxide in the presence of acetic acid. Analyses of the salt were made by J. F. W. Herschel, P. Jochum, C. F. Rammelsberg, J. Fogh, A. Gutmann, and W. H. Perkins and A. T. King. Lead thiosulphate appears as a white crystalline powder which is stable in air at ordinary temp., but, according to J. F. W. Herschel, it blackens when heated to 100°, and when heated more strongly with the exclusion of air it forms lead sulphide and sulphate with the evolution of sulphur dioxide. C. F. Rammelsberg found that some sulphur is also formed, and that while the thiosulphate remains white at 100°, it darkens at 200°. C. Pape observed that in air decomposition sets in just over 100°, and P. Jochum, near 120°. C. Pape gave 5·58° for the rotary polarization of the crystals. According to J. F. W. Herschel, 100 parts of water dissolve 0·0326 part of salt ; C. F. Rammelsberg said 0·03 part ; and P. Jochum, traces. Boiling water decomposes the thiosulphate, and after a prolonged boiling, F. J. Faktor, P. Jochum, and W. H. Perkins and A. T. King found that lead sulphide is formed. When heated in the presence of water in a sealed tube, at 140°, J. T. Norton represented the reaction : $4PbS_2O_3=PbS+4S+3PbSO_4$, with traces of hydrogen sulphide ; and with an excess of a soln. of sodium thiosulphate, in a sealed tube, W. H. Perkins and A. T. King represented the reaction : $PbS_2O_3+3Na_2S_2O_3=PbS+4S+3Na_2SO_4$. J. Fogh found that when dil. soln. of lead acetate and sodium thiosulphate are mixed, the lead is completely precipitated in the form of anhydrous thiosulphate, PbS_2O_3, with development of +5·8 Cals. at 10°. This corresponds with +8·6 Cals. for the solid acetate and thiosulphate. The lead thiosulphate immediately after precipitation dissolves completely in a soln. of sodium thiosulphate with absorption of −0·392 Cal. at 11°. The dried precipitate requires a stronger soln. of the sodium salt for rapid soln., but the absorption of heat (−0·418 Cal.) is practically the same, and hence the physical condition of the thiosulphate is not changed during the process of washing and drying. It follows that as the heats of formation of lead acetate and sodium acetate and thiosulphate from their elements are known, the heat of formation of the lead thiosulphate from its elements can be calculated. Taking the heat of formation of dissolved thiosulphuric acid as +79·4 Cal. (Pb,2S,3O)=152 Cals. A. Slator gave $1·5\times10^{-4}$ for the ionization constant: $[Pb^{\cdot\cdot}][S_2O_3'']=K[PbS_2O_3]$. J. Fogh said that the dried thiosulphate dissolves very slowly in alkali thiosulphate soln.; and complex salts are formed. According to T. Fakamatsu and W. Smith, a dil. soln. of iodine in hydriodic acid forms tetrathionic acid, and a conc. soln., pentathionic acid. C. W. Blomstrand represented the reaction with phosphorus pentachloride by: $2PCl_5+PbS_2O_3=PbCl_2+POCl_3+PSCl_3+SO_2Cl_2$. The reaction was studied by C. Pape, and J. Y. Buchanan.

C. F. Rammelsberg dissolved lead thiosulphate in a lukewarm, conc. soln. of ammonium thiosulphate, with shaking, and on evaporation obtained transparent, rhombic plates of **ammonium lead trithiosulphate,** $2(NH_4)_2S_2O_3.PbS_2O_3$. If the temp. is too high lead sulphide is formed, and this is also the case if the soln. be allowed to evaporate spontaneously. The salt is freely soluble in cold water, and the soln. quickly becomes turbid, forming lead sulphide and sulphate. A. Ferratini obtained **hydrazine lead thiosulphate,** $2(N_2H_4)H_2S_2O_3.PbS_2O_3.H_2O$, in rectangular plates by treating a lukewarm soln. of lead chloride with hydrazine thiosulphate—not in excess or the precipitate will dissolve. The precipitate is successively washed with aq. alcohol, and alcohol. At 100°, the salt becomes brown; it melts at 122°–123°, forming a brown liquid; it is insoluble in water and alcohol, but soluble in dil. nitric or hydrochloric acid. Fuming nitric acid forms lead sulphate. J. Meyer and H. Eggeling obtained crystals of **lithium lead dithiosulphate,** $Li_2S_2O_3.PbS_2O_3$, by evaporating over sulphuric acid a soln. of the component salts to a small vol., filtering, and evaporating over sulphuric acid in vacuo in darkness. The hygroscopic crystals quickly decompose when moist, and lead sulphide is formed. A. and L. Lumière and A. Seyewetz found that a soln. of sodium thiosulphate dissolves lead sulphate, and chloride; P. Jochum, lead; and E. H. Russell, and C. A. Stetefeldt, lead sulphate, but not lead chloride. According to J. Fogh, sodium lead thiosulphate is produced by mixing soln. of sodium thiosulphate and lead acetate, and adding alcohol to the mixture. If the soln. are conc., the liquid separates into two layers, and when the lower layer is treated with more alcohol, it solidifies to a white, amorphous mass of variable composition. The heat of soln. of this product indicates that it is a mixture of lead sodium thiosulphate and hydrated sodium thiosulphate, and it is probable that some of the complex lead sodium thiosulphates previously described were really mixtures of the same kind. If the soln. are dil., a white, gelatinous precipitate forms and gradually changes to crystalline plates. When dried in vacuo, the crystals are **sodium lead trithiosulphate,** $PbS_2O_3.2Na_2S_2O_3$. The heat of soln. of this compound in a dil. soln. of sodium thiosulphate is —4·1 Cals. at 10°, and hence its heat of formation from its constituent salts is 5·3 Cals. This compound was also prepared by P. Jochum, and C. Lenz. P. Jochum said that the salt decomposes at 30°–40° in air; and C. F. Rammelsberg, that out of contact with air, sulphur dioxide and sulphur are given off, while a mixture of potassium and lead sulphides and sulphates remains. C. Lenz found that the salt is sparingly soluble in water, readily soluble in a soln. of sodium acetate; and F. Field, that a mixed soln. of sodium thiosulphate and sulphate gives no precipitate with lead nitrate, and when the soln. is heated, lead sulphide is precipitated. The salt is soluble in a soln. of sodium thiosulphate, and, according to A. and L. Lumière and A. Seyewetz, A. Jouve, and J. W. Slater, the soln. is decomposed very slowly in light, and rapidly when boiled, depositing lead sulphide. A. Slator measured the rate of reaction of lead thiosulphate with ethyl bromoacetate. P. Jochum reported that **sodium lead heptathiosulphate,** $5Na_2S_2O_3.2PbS_2O_3.60H_2O$, is formed in a mass of scaly crystals, by adding alcohol to a mixture of a cold conc. soln. of lead acetate and sufficient sodium thiosulphate to dissolve the precipitate first formed; but J. Fogh, and G. Vortmann and C. Padberg showed that it is not a chemical individual but rather a mixture. G. Vortmann and C. Padberg added alcohol to a mixed soln. of lead acetate and an excess of sodium thiosulphate sufficient to dissolve the precipitate first formed, and obtained white crystals of **sodium lead tetrathiosulphate,** $3Na_2S_2O_3.PbS_2O_3.12H_2O$. They measured the e.m.f. of soln. of this complex salt; and found the ionization constant $\sqrt{K}=2{\cdot}5\times10^{-4}$ for $[Na_2S_2O_3]^2[Pb^{\cdot\cdot}][S_2O_3{}'']^2 = K[Na_2Pb(S_2O_3)_4$. J. Fogh regarded this salt as a mixture; and he also made a similar remark with respect to **sodium lead pentathiosulphate,** $4Na_2S_2O_3.PbS_2O_3.15H_2O$, obtained by adding a conc. soln. of lead acetate to a soln. of sodium thiosulphate until a turbidity appears, adding alcohol, and allowing the product to dry in vacuo. C. F. Rammelsberg prepared **potassium lead trithiosulphate,** $2K_2S_2O_3.PbS_2O_3.2H_2O$, in needle-like crystals, as in the case of the corresponding ammonium salt. W. Spring found that when the aq. soln. is boiled, lead sulphide is precipitated, and potassium trithionate passes into soln. J. Mayer and H. Eggeling obtained **rubidium lead trithiosulphate,** $2Rb_2S_2O_3.PbS_2O_3.2H_2O$, in a similar way; likewise also with **cæsium lead trithiosulphate,** $2Cs_2S_2O_3.PbS_2O_3.2H_2O$, which was obtained as the second crop of crystals from a hot, filtered soln. of lead thiosulphate in a warm, conc. soln. of cæsium thiosulphate; the first crop of needle-like crystals was **cæsium lead dithiosulphate,** $Cs_2S_2O_3.PbS_2O_3.2H_2O$. C. F. Rammelsberg found that a clear green precipitate is obtained by mixing soln. of cupric acetate and potassium lead thiosulphate. It quickly turns brown when allowed to stand in its mother-liquid, or exposed to air. J. de Girard obtained a white precipitate under similar conditions with sodium lead thiosulphate and a conc. soln. of lead acetate. The resulting **cuprous lead dithiosulphate,** $Cu_2S_2O_3.PbS_2O_3.3H_2O$, or $Pb(CuS_2O_3)_2.3H_2O$, is freely soluble in water, and rapidly decomposes into cuprous and lead sulphides. C. F. Rammelsberg prepared **calcium lead trithiosulphate,** $2CaS_2O_3.PbS_2O_3.4H_2O$, in white crystals, by adding alcohol to a soln. of the component salts; similarly with **strontium lead thiosulphate,** and with **barium lead thiosulphate.**

W. Farmer and J. B. Firth[15] obtained **sodium arsenothiosulphate,** presumably $Na_3As(S_2O_3)_3$, as an intermediate compound in the reduction of the arsenohyposulphite to arsenic trisulphide. A. Carnot, and O. Hauser were unable to prepare **bismuth thiosulphate,** but complex salts of the type $R_3Bi(S_2O_3)_3.nH_2O$ were readily obtained. O. Hauser showed that soln. of these salts contained the complex anion $Bi(S_2O_3)'''$, which breaks up comparatively easily. K. A. Hofmann and F. Höchtlen also prepared **ammonium bismuth decasulphodithiosulphate,** $(NH_4)_4Bi_2(S_2O_3)_2S_{10}$, by shaking together soln. of ammonium polysulphide and bismuth chloride in absolute alcohol, and allowing the mixture to stand at 5°. The black crystals were washed successively with alcohol, ether, carbon disulphide, and ether, and dried in vacuo over sulphuric acid. The supposed constitution is: $(NH_4S_4)(NH_4S_2O_3):Bi.S.S.Bi:(NH_4S_4)(NH_4S_2O_3)$.

No report of **arsenic thiosulphate** has yet appeared. G. Vortmann[16] found that in the presence of a sufficient excess of sodium thiosulphate, arsenic trioxide is completely converted into the sulphide, and the filtrate contains chiefly tetrathionic acid, together with traces of pentathionic acid. With arsenic trioxide in excess, however, the reaction is expressed by the equation $As_2O_3+9H_2S_2O_3 = As_2S_3+3H_2S_4O_6+3SO_2+6H_2O$. Arsenic acid and sodium thiosulphate yield arsenic trisulphide, together with much pentathionic acid and traces of sulphuric acid. According to J. von Szilagyi, no complex salts have been made with sodium, rubidium, or cæsium, but barium seems to form an unstable **barium arsenious thiosulphate,** $Ba_3\{As(S_2O_3)_3\}_2$, existing only in soln. W. Farmer and J. B. Firth prepared **sodium arsenious thiosulphate,** $Na_3As(S_2O_3)_3$, as follows: equi-normal soln. of potassium hydroxide, and hydrochloric acid were prepared; 25 c.c. of the standard alkali, in which a gram of sodium arsenious hyposulphite (1 mol) and the calculated quantity of sodium sulphite (3 mols) had been dissolved, were rapidly added to 25 c.c. of the standard acid containing 2·5 c.c. of conc. acid. A turbidity developed, followed by precipitation of arsenious sulphide. Decomposition of sodium arsenious hyposulphite in presence of sodium sulphite by this neutralization method is considered to the lead to formation, and rapid decomposition, of sodium arsenothiosulphate, arsenious sulphide being one of the products. J. von Szilagyi prepared **potassium arsenious thiosulphate,** $K_3As(S_2O_3)_3$, as a white, amorphous solid, by adding a soln. of 37·24 grms. of crystallized sodium thiosulphate in 60 c.c. of water to a soln. of 4·95 grms. of arsenious oxide in 35 c.c. of hydrochloric acid of sp. gr. (1·06) and 11·18 grms. of potassium chloride in 30 c.c. of water at 3°. Three volumes of 96 per cent. alcohol are added to the mixture, when the double salt is precipitated. It is rapidly filtered and washed with alcohol and ether. It is a pure white compound, which is not very stable in the moist condition ; it is amorphous, and is very soluble in water, slightly soluble in 50 per cent. alcohol, and insoluble in absolute alcohol, ether, and chloroform. The sp. gr. is 2·292 at 18°/4°. When quite dry, it may be preserved, but when moist, even with chloroform or ether, it becomes yellow. When the dry salt is heated, it decomposes according to the equation $2K_3As(S_2O_3)_3=As_2S_3+3K_2SO_4+3SO_2+3S$; on keeping or boiling a soln. of the salt it decomposes according to the equation $2K_3As(S_2O_3)_3 \rightleftharpoons As_2S_3+3K_2S_3O_6$. F. V. von Hahn failed to prepare a colloidal soln. of arsenic pentasulphide by the hydrolysis of the alkali arsenious thiosulphate. G. Canneri obtained **thallous arsenious thiosulphate,** $Tl_3As(S_2O_3)_3$, by the method used for the corresponding bismuth salt. The white compound readily decomposes when moist : $2Tl_3As(S_2O_3)_3=As_2O_3+3Tl_2S_2O_3$; $2Tl_2S_2O_3+2H_2O=2Tl_2S+2H_2SO_4$; and $Tl_2S+H_2SO_4=H_2S+Tl_2SO_4$. No **antimony thiosulphate** has been prepared ; G. Vortmann found that the action of sodium thiosulphate on antimony trichloride corresponds with that on arsenious acid ; the filtrate from the antimony trisulphide contains only traces of sulphuric acid, but much tetrathionic acid. F. J. Faktor also observed that a red oxysulphide, $SbSO_2$, is precipitated by boiling a soln. of potassium antimonyl tartrate and sodium thiosulphate ; and when exposed to sunlight it forms Sb_2SO_4. The same product is obtained by mixing boiling soln. of the two salts. J. von Szilagyi obtained a series of complex salts by adding a soln. of antimony trioxide in hydrochloric acid (sp. gr. 1·12) to a soln. of sodium thiosulphate and the chloride of the metal concerned at low temp., about 3°. The formation is represented by the equations : $SbCl_3+H_2O=SbOCl+2HCl$; $SbOCl+2HCl+3Na_2S_2O_3=3NaCl+H_2O+Na_3Sb(S_2O_3)_3$. The salts in all cases, except those of sodium, calcium, and strontium, may be crystallized at low temp., and are precipitated by the addition of 96 per cent. alcohol. Their structure can be represented by $Sb(S.SO_2.OK)_3$, or $Sb(O.SO_2.SK)_3$. **Sodium antimonious thiosulphate,** $Na_3Sb(S_2O_3)_3$, is very soluble and has not been obtained in the solid state ; and when the attempt is made to isolate the compound it decomposes : $2Na_3Sb(S_2O_3)_3=3Na_2S_2O_3+Sb_2OS_2+4SO_2$. F. V. von Hahn prepared a colloidal soln. of antimony pentasulphide (*q.v.*) by the hydrolysis of the sodium salt : $2Na_3Sb(S_2O_3)_3=Sb_2S_5+3Na_2SO_4+3SO_2+S$. **Potassium antimonious thiosulphate,** $K_3Sb(S_2O_3)_3$, forms silk-like, needle-shaped crystals very similar in appearance to asbestos. It is very soluble in water, and on diluting the soln. a very slight turbidity is produced which points to the presence of the complex ion, $Sb(S_2O_3)_3'''$. On boiling a soln. decomposition occurs, forming the orange-red compound, Sb_2OS_2, as in the case of the sodium compound. On heating the crystals above 100°, the decomposition $2K_3Sb(S_2O_3)_3=Sb_2S_3+3K_2SO_4+3SO_2+3S$ takes place. It was not possible to isolate **calcium antimonious thiosulphate** and **strontium antimonious thiosulphate,** because they are stable even in soln. for only a short time. **Barium antimonious thiosulphate,** $Ba_3\{Sb(S_2O_3)_3\}_2$, is not very stable at the moment of precipitation ; it is white, but speedily becomes yellow owing to decomposition. G. Canneri prepared **thallous antimonious thiosulphate,** $Tl_3Sb(S_2O_3)_3$, as a white, crystalline powder, by the method used for the bismuth salt. It is stable in dry air, but reddens in moist air owing to the reaction : $2Tl_3Sb(S_2O_3)_3 \rightleftharpoons Sb_2OS_2+4SO_2+3Tl_2S_2O_3$.

F. J. Faktor found that neutral aq. soln. of bismuth salts are quantitatively precipitated by boiling with sodium thiosulphate. O. Hauser showed that **sodium**

bismuth thiosulphate, $Na_3Bi(S_2O_3)_3$, is formed when bismuth nitrate is rubbed with excess of sodium thiosulphate. The product is extracted with a mixture of alcohol and water (1 : 1); on addition of more alcohol, the salt is precipitated as a yellow oil; which, when placed over sulphuric acid under reduced press., gives orange-yellow crystals. The salt is unstable in the dry state, but keeps fairly well in alcoholic aq. soln. When a soln. of potassium chloride and one of sodium thiosulphate is added to a cooled soln. of bismuth oxide in hydrochloric acid, yellow, prismatic crystals of **bismuth potassium thiosulphate,** $K_3Bi(S_2O_3)_3.\frac{1}{2}H_2O$, separate. One hundred c.c. of soln., sat. at 2°, contain 3·5 grms. of the salt, and at 18°, about 7 grms. In a vacuum over phosphoric oxide, the anhydrous salt is formed. The aq. soln. rapidly decomposes, but soln. containing alkali salts are stable. Sodium thiosulphate soln. dissolves more of the salt than does pure water. The thiosulphate group in the salt cannot be titrated with iodine. The precipitate of this salt may be used for the detection of potassium, but cannot serve for its quantitative estimation. The salt was also prepared by V. Cuisinier. L. Vanino and F. Mussgnug obtained small octahedra of stable salt by the interaction of a bismuth-mannitol soln. and sodium thiosulphate in the presence of manganese chloride. A. Carnot proposed the use of an alcoholic soln. of sodium bismuth thiosulphate as a precipitant for potassium from say a soln. of potassium chloride. The merits of this reagent for precipitating potassium in the form of potassium bismuth thiosulphate were also examined by G. Campari, C. Pauly, and H. Weber. According to O. Hauser, yellow **bismuth rubidium thiosulphate,** $Rb_3Bi(S_2O_3)_3.\frac{1}{2}H_2O$, is formed in the same way as the potassium salt. It forms a yellow, crystalline powder which loses its water of crystallization over phosphoric oxide in a vacuum. When this salt is treated with a small quantity of ice-water, it becomes brown with formation of the salt $Rb_3Bi(S_2O_3)_3,H_2O$. When sodium thiosulphate is mixed with a soln. containing cæsium nitrate and bismuth nitrate in nitric acid and then alcohol added, a yellow, crystalline powder of **bismuth cæsium thiosulphate,** $Cs_3Bi(S_2O_3)_3$, is deposited. It is more stable than the potassium or rubidium salts. L. Vanino and F. Mussgnug prepared **ammonium bismuth thiosulphate,** $(NH_4)_3Bi(S_2O_3)_3$, as a yellow precipitate which soon changes colour, and is decomposed by water. The **copper bismuth thiosulphate,** $Cu_3\{Bi(S_2O_3)_3\}_2$, is precipitated only after adding alcohol; **silver bismuth thiosulphate,** $Ag_3Bi(S_2O_3)_3$, forms a yellow precipitate which rapidly blackens. **Barium bismuth thiosulphate,** $Ba_3[Bi(S_2O_3)_3]_2$, is formed in the same way as the potassium salt; it is hydrolyzed very easily. Indistinctly crystalline **strontium bismuth thiosulphate,** $Sr_3\{Bi(S_2O_3)\}_2$, obtained by L. Vanino and F. Mussgnug, is hydrolyzed by water. G. Canneri prepared **thallous bismuth thiosulphate,** $Tl_3Bi(S_2O_3)_3$, either from the complex sodium thallous trithiosulphate and bismuth chloride, or from potassium bismuth thiosulphate and a thallous salt. It forms a sparingly soluble, microcrystalline, yellow powder. It is moderately stable in neutral soln. at a low temp., but decomposes with formation of sulphur dioxide and bismuth sulphide when gently heated, the decomposition being retarded by alcohol and accelerated by a trace of acid. The salt is soluble in excess of potassium bismuth thiosulphate soln., yielding a clear liquid, with which alcohol forms a microcrystalline, orange-yellow precipitate containing both thallium and potassium.

No **chromium thiosulphate** has been prepared, but P. C. Ray and P. B. Sarkar[17] obtained **chromium aquotrihydroxydioldecamminothiosulphate,** $[Cr(OH)_3.2Cr(OH)(NH_3)_5.H_2O](S_2O_3)_2.nH_2O$, in reddish-violet crystals and **chromium diaquotrihydroxydiolenneaminothiosulphate,** $[Cr(OH)_3.Cr(OH)(NH_3)_5.Cr(OH)(NH_3)_4H_2O.H_2O](S_2O_3)_2.2H_2O$, in pinkish-violet crystals. According to F. J. Faktor, when a soln. of potassium chromate or dichromate, mixed with ammonium or magnesium chloride, is boiled with an excess of sodium thiosulphate, the chromium is precipitated quantitatively as chromium chromate mixed with a little sulphur. A soln. of chromic chloride does not give a quantitative precipitate unless a little chromate is also present. A mixture of sodium thiosulphate and hydrogen dioxide reduces chromates to chromic hydroxide. No **molybdenum thiosulphate** has been reported. A soln. of sodium thiosulphate reduces ammonium molybdate to molybdenum trioxide and the hydrated dioxide. No **tungsten thiosulphate** has been prepared. Sodium tungstate with a warm soln. of sodium thiosulphate, and a little nitric acid, yields a mixture of tungsten dioxide, trioxide, and heptoxide. Soln. of uranyl nitrate and sodium thiosulphate furnish a yellow precipitate of **uranyl thiosulphate,** $(UO_2)S_2O_3$—*vide* uranous chloride.

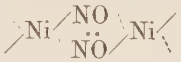
G. Vortmann and C. Padberg[18] triturated barium thiosulphate with a conc. soln. of manganese sulphate, added alcohol and ether to the filtered soln., and allowed it to crystallize. An aq. soln. of the **manganous thiosulphate,** $MnS_2O_3.5H_2O$, deposits manganese sulphide when boiled. By this method, A. Fock and K. Klüss obtained an oily liquid which decomposed in vacuo. C. F. Rammelsberg also found that the filtrate from mixed soln. of barium thiosulphate and manganese sulphate decomposed when evaporated in air or over conc. sulphuric acid. C. F. Rammelsberg, and A. Guerout observed the formation of some manganese thiosulphate when sulphur dioxide is passed into water with manganese sulphide in suspension; if the sulphur dioxide be not in excess, the sulphite is formed. For W. E. Henderson and H. B. Weiser's observations on the formation of this salt, *vide supra,* zinc thiosulphate. P. Jochum obtained **sodium manganous trithiosulphate,** $2Na_2S_2O_3.MnS_2O_3.16H_2O$, in steel-blue crystals, by adding a mixture of alcohol and ether (1 : 2) to a mixed soln. of the component salts. G. Vortmann and C. Padberg's product, obtained in a similar way, was pale rose-coloured. The salt is soluble in water and in aq. alcohol, but not in absolute alcohol; it decomposes in air, forming manganese sulphide, and the decomposition is rapid at 40°. The soln. decomposes on boiling; and ammonia or potash-lye gives a flesh-coloured precipitate.

According to C. L. Berthollet,[19] when iron is immersed in sulphurous acid, out of contact with air, it dissolves without evolving gas, forming ferrous sulphite and thiosulphate: $2Fe+3H_2SO_3=FeSO_3+FeS_2O_3+3H_2O$, and the iron becomes black and brittle by taking up sulphur. M. J. Fordos and A. Gélis said that the metal dissolves completely in the acid except for a few black flakes arising from impurities. A. Vogel, and C. J. Koene found that the sulphurous acid first becomes brown, then yellow, and afterwards transparent and colourless owing to the precipitation of sulphur. No hydrogen sulphide is evolved, but the liquid contains a small portion of that gas while it is in the yellow stage. If conc. sulphurous acid be used, some of the sulphite crystallizes spontaneously from the soln. in a few days; and M. J. Fordos and A. Gélis added that if the soln. be evaporated and cooled out of contact with air, the greater part of the sulphite can be crystallized out, and the mother-liquor, when evaporated at ordinary temp. in vacuo, yields crystals of **ferrous thiosulphate,** $FeS_2O_3.5H_2O$, frequently contaminated with sulphur and ferrous sulphate. For, if any air has had access to the mother-liquid, yellow ferric thiosulphate is formed, which, on evaporation, forms ferrous tetrathionate, which breaks down into ferrous sulphate, sulphur dioxide, and sulphur. C. J. Koene separated the sulphite and thiosulphate by washing the product with 98 per cent. alcohol—in which the thiosulphate is soluble, the sulphite insoluble; allowing the alcoholic soln. to stand a couple of days in contact with iron ribbon; and evaporating the pale green alcoholic soln. in vacuo over sulphuric acid. For the preparation of ferrous thiosulphate from the sulphide and sulphurous acid by W. E. Henderson and H. B. Weiser, *vide supra,* zinc thiosulphate. C. F. Rammelsberg prepared the salt by double decomposition with barium thiosulphate and ferrous sulphate soln., and evaporating the filtrate. The green crystals may be mixed with some basic ferric thiosulphate. The ferrous salt is also formed when sulphur acts on a soln. of ferrous sulphate; though G. Vortmann and C. Padberg found that soln. of iron sulphate are not altered when boiled with sulphur. The bluish-green crystals of ferrous thiosulphate are very hygroscopic; they are stable if protected from air, but they very readily oxidize, forming a basic ferric hyposulphite as indicated above. In contact with iron, sulphur and sulphurous acid are formed. F. J. Faktor observed that soln. of ferrous salts are not precipitated on boiling with sodium thiosulphate unless ammonium chloride and ammonia are added. The iron then gradually separates as sulphide. W. Feld said that ferrous thiosulphate, free from sodium salts, is prepared by passing hydrogen sulphide into a cold soln. of ferrous sulphate and sodium thiosulphate. The precipitate of ferrous sulphide and sulphur is collected, washed with cold boiled water, suspended in water, and added slowly to water through which sulphur dioxide, diluted with hydrogen, is passed, the mixture of gases being made more dilute as the operation proceeds. The reactions occurring are: (i) $2FeS+3SO_2=2FeS_2O_3+S$; (ii) $FeS+3SO_2-FeS_4O_6$; (iii) $FeS+3SO_2 \quad FeS_3O_6+S$. A further quantity of the sulphide is then added to remove excess of sulphur dioxide, the polythionates being reduced at the same time: (iv) $FeS_4O_6+FeS=2FeS_2O_3+S$; (v) $FeS_3O_6+FeS=2FeS_2O_3$. Hydrogen sulphide was found by R. F. Carpenter and E. Linder to form iron disulphide; but, added W. Feld, the reaction is complete only in hot soln. G. Vortmann and C. Padberg obtained **sodium ferrous thiosulphate,** $3Na_2S_2O_3.FeS_2O_3.8H_2O$, in bright green crystals, by precipitating a mixed soln. of ferrous iodide and sodium thiosulphate with alcohol. The salt is very soluble in water, and easily decomposed. According to A. Vogel, an insoluble **ferric thiosulphate** can be obtained in greenish-white octahedra, by immersing steel turnings for 14 days in conc. sulphurous acid, in a closed vessel, for 14 days, pouring off the colourless liquor, and washing the turnings with water. The crystals adhere to the surface of the metal. The crystals do not fuse when heated, but evolve sulphur dioxide and a little sulphur; they become opaque and rust-coloured on exposure to air; they effervesce with the evolution of sulphur dioxide when treated with hydrochloric acid, and the resulting yellow liquid deposits sulphur; and they are insoluble in hot or cold water, but they are dissolved slowly by sulphurous acid. F. J. Faktor found that neutral soln. of ferric salts are first coloured violet by sodium thiosulphate, but gradually assume a yellow or brownish-yellow colour, which is not altered on prolonged boiling. If, however, a little ammonia is added, a greenish-black precipitate is formed, which on continued boiling yields blackish-brown, granular, ferrosic hydroxide. The precipitation does not seem to be complete. J. Holluta and A. Martini represented the mechanism of the reduction of ferric salts by sodium thiosulphate as follows: (i) $Fe^{\cdot\cdot\cdot}+2HS_2O_3{}'\rightleftharpoons[Fe(S_2O_3)_2]'+2H^{\cdot}$; (ii) $[Fe(S_2O_3)_2]'+Fe^{\cdot\cdot\cdot}=2Fe^{\cdot\cdot}+S_4O_6{}''$; (iii) $H^{\cdot}+S_4O_6{}''=HS_4O_6{}'$. The reaction is retarded by the addition of acids in a similar way to the action of neutral salts; with an excess of acid, the reaction (i) goes from right to left, whereas a small amount of acid (0·05 mol per litre) increases the conc. of the ferric ions by repressing hydrolysis and consequently accelerating reaction (ii). As the acidity of the soln. increases, a side reaction of the fourth order commences to take place, thus, (iv) $2Fe^{\cdot\cdot\cdot}+2HS_2O_3{}'=2Fe^{\cdot\cdot}+HS_4O_6{}'+H^{\cdot}$, and when the acidity exceeds $0{\cdot}5N$ this becomes the sole reaction that takes place. With very high acidity, the thiosulphate slowly decomposes into sulphite and sulphur and the velocity constant of (iv) rapidly falls.

C. F. Rammelsberg obtained **cobalt thiosulphate,** $CoS_2O_3.6H_2O$, by treating a soln. of cobalt sulphate with strontium thiosulphate, and evaporating the filtrate at a gentle heat. Towards the end of the evaporation, the liquid turns blue, and becomes turbid through the deposition of sulphur; and finally it furnishes red, prismatic crystals, which, according to A. Fock and K. Klüss, are triclinic with the axial ratios $a:b:c=0{\cdot}8381:1:0{\cdot}7360$, and $\alpha=91° 52'$; $\beta=92° 2'$; and $\gamma=83° 28'$. The salt was also made by E. A. Letts. G. Vortmann and C. Padberg obtained **sodium cobalt tetrathiosulphate,** $3Na_2S_2O_3.CoS_2O_3.15H_2O$, by adding alcohol to a mixed soln. of cobalt chloride and sodium thiosulphate; the precipitated oily liquid dries in a desiccator to a gummy mass. P. Jochum also reported **sodium cobalt heptathiosulphate,** $5Na_2S_2O_3.2CoS_2O_3.25H_2O$, prepared in an analogous manner, but G. Vortmann and C. Padberg were unable to confirm its existence. P. R. Ray prepared **cobaltic thiosulphatopentamminothiosulphate,** $[Co(NH_3)_5(S_2O_3)]_2S_2O_3.H_2O$, by the passage of a current of air into a soln. of cobalt hydroxide, ammonium thiosulphate, and ammonia. The purple crystals are sparingly soluble in water, and are decomposed by mineral acids; when treated with an excess of ethylendiamine at 60°, soluble, yellow **cobaltic trisethylenediamminothiosulphate,** $[Co\ en_3]_2(S_2O_3)_3$, is formed. The filtrate remaining after the separation of the thiosulphatopentamminothiosulphate, was treated with a current of air until it no longer smelt of ammonia. After standing some time, it deposited yellowish brown crystals of **cobaltic sulphitopentamminothiosulphate,** $[Co(NH_3)_5SO_3]_2S_2O_3$, and a hemitrihydrated variety was also formed. When a current of air is passed through an ammoniacal soln. of cobalt chloride, ammonium chloride, and sodium thiosulphate, yellow crystals of **cobaltic hexamminochlorothiosulphate,** $[Co(NH_3)_6]Cl(S_2O_3)$, are formed; if a larger proportion of ammonium chloride and less thiosulphate are employed, **cobaltic thiosulphatopentamminochloride,** $[Co(NH_3)_5(S_2O_3)]Cl$, is formed. When this salt is treated with sodium bromide, red crystals of **cobaltic thiosulphatopentamminobromide,** $[Co(NH_3)_5(S_2O_3)]Br$, are formed; and with potassium iodide, **cobaltic thiosulphatopentamminoiodide,** $[Co(NH_3)_5(S_2O_3)]I$, is formed. If the cobaltic pentamminothiosulphate be treated with a soln. of potassium cyanide, *potassium pentacyanidothiosulphate,* $K_4[Co(S_2O_3)(CN)_5]$, is formed; and if treated with a warm conc. soln. of sodium nitrite, cobaltic triamminotrinitrite, $[Co(NO_2)_3(NH_3)_3]$, is formed. When air is passed into an ammoniacal soln. of cobalt nitrate, ammonium nitrate, and sodium thiosulphate, purple-red crystals of **cobaltic thiosulphatopentamminonitrate,** $[Co(NH_3)_5(S_2O_3)]NO_3$, are formed; and if sodium dithionate is added to a 4 per cent. ammonia soln. of the nitrate, purple-red crystals of **cobaltic thiosulphatopentamminodithionate,** $[Co(NH_3)_5(S_2O_3)]_2S_2O_6$, are formed. When potassium chromate is added to a soln. of the chloride, red, silky needles of **cobaltic thiosulphatopentamminochromate,** $[Co(NH_3)_5(S_2O_3)]_2CrO_4$, are formed. Air passed through an ammoniacal soln. of cobalt hydroxide, ammonium thiosulphate, and sodium nitrite furnishes brownish-yellow crystals of **cobaltic nitritopentamminothiosulphate,** $[Co(NH_3)_5(NO_2)]S_2O_3$. F. J. Faktor observed that when cobalt salts are treated with a mixture of sodium thiosulphate and hydrogen dioxide, a black precipitate is formed. P. R. Ray prepared some thiosulphatocyanides.

F. J. Faktor found that when nickel salts are treated with a mixture of sodium thiosulphate and hydrogen dioxide, a pale green precipitate is formed. When boiled with a soln. of sodium thiosulphate, nickel and cobalt salts give the sulphides, but the precipitation is never complete. According to M. J. Fordos and A. Gélis, nickel, like zinc, dissolves in sulphurous acid, without the evolution of gas, forming nickel sulphite and hyposulphate. The green soln. on evaporation, deposits crystals of the sulphite, and afterwards crystals of **nickel thiosulphate,** $Ni_2S_2O_3.6H_2O$, while the mother-liquor is resolved by heat into sulphur, and nickel sulphide and sulphate. C. F. Rammelsberg evaporated over sulphuric acid the filtrate from a mixed soln. of strontium hyposulphate and nickel sulphate. There is a slight decomposition of the liquid attended by the separation of nickel sulphide. The crystals yield a semi-fluid mass below 100°, and as the temp. rises give off water, sulphur, and sulphur dioxide leaving a residue of nickel sulphides. The salt was also made by E. A. Letts. According to C. F. Rammelsberg, if a conc. soln. of the salt be sat. with ammonia, and the blue liquid treated with alcohol, crystals of **nickel tetramminothiosulphate,** $NiS_2O_3.4NH_3.6H_2O$, are formed; F. Ephraim gave $NiS_2O_3.5NH_3.H_2O$; and G. Vortmann and C. Padberg, $Ni_2S_2O_3.6NH_3.3H_2O$. The blue crystalline powder soon turns green on exposure to air. P. Jochum reported pale green plates of **sodium nickel heptathiosulphate,** $5Na_2S_2O_3.2NiS_2O_3.25H_2O$, to be formed by adding alcohol to an ammoniacal soln. of a nickel salt mixed with sodium thiosulphate. L. Cambi and A. Clerici studied the action of nitric oxide on nickel thiosulphate, and also prepared **potassium nickel nitrosyl-**

thiosulphate, $K_3[(NO)Ni(S_2O_3)_2].2H_2O$; it is here assumed that the salt contains a hyponitrous residue :



P. Schottländer[20] dissolved ammonium chloroplatinate in a conc. aq. soln. of sodium thiosulphate, and found that the clear soln. soon became turbid and deposited platinum mixed with sulphur. If alcohol be added to the clear soln., a yellow oil is precipitated which forms a mass of yellow crystals of **sodium platinous tetrathiosulphate,** $3Na_2S_2O_3.PtS_2O_3.10H_2O$. P. Jochum obtained a similar salt. The orange-yellow crystalline mass decomposes at 100°. It is freely soluble in water ; and the soln. is not changed by boiling with soda-lye. Hydrogen sulphide gives no precipitate with the neutral soln. or the cold soln. acidified with hydrochloric acid. Hydrochloric acid very slowly decomposes the cold soln. and more quickly when heated giving off sulphur dioxide and depositing platinic disulphide. P. Jochum precipitated the yellow oil as indicated above, allowed it to crystallize under absolute alcohol, and thus obtained **sodium platinous pentathiosulphate,** $4Na_2S_2O_3.PtS_2O_3.10H_2O$. He also obtained yellow needles of **sodium platinous heptathiosulphate,** $6Na_2S_2O_3.PtS_2O_3.19H_2O$, by neutralizing as nearly as possible a soln. of hydrochloroplatinic acid with sodium carbonate, adding an equal vol. of a conc. soln. of sodium thiosulphate, precipitating with alcohol, and crystallizing under absolute alcohol. C. Rudelius reported *platinum dipropylsulphinodithiosulphate,* $[Pt\{(C_3H_7)_2S\}_2(S_2O_3)_2]$.

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§ 39. The Polythionic Acids

The **polythionic acids** are taken to include a series of acids with the general formula $H_2S_nO_6$, where n ranges from 2 to possibly 6 ; for example, there are : dithionic acid, $H_2S_2O_6$; trithionic acid, $H_2S_3O_6$; tetrathionic acid, $H_2S_4O_6$; pentathionic acid, $H_2S_5O_6$; and hexathionic acid, $H_2S_6O_6$. They are formed when sulphur dioxide, water, and sulphur *in statu nascendi* react with one another under different conditions. J. Dalton [1] observed that when moist sulphur dioxide and hydrogen sulphide react on one another in the gaseous state, or in aq. soln., they produce an acid which he thought to be represented by the particles causing the turbidity of the liquid. J. Dalton said :

> When sulphuretted hydrogen and sulphurous acid are mixed over mercury in the proportion of six measures of the former to five of the latter, both gases lose their elasticity, and a solid is deposited on the sides of the tube. The common explanation given of this fact is that the hydrogen of one gas unites to the oxygen of the other to form water, and the sulphur of both gases is precipitated. This explanation is not correct ; water is indeed formed, as stated ; but the deposition consists of a mixture of solid bodies, the one sulphur, the other sulphurous oxide ; they may be distinguished by their colour ; the former is yellow, the latter bluish-white, and when they are both thrown into water, the former soon falls down, but the latter remains for a long time suspended in the water and gives it a milky appearance, which it retains after filtration. Again, if water impregnated with each of the gases, be mixed together till a mutual saturation takes place or until the smell of neither gas is observed after agitation, a milky liquid is obtained which may be kept for some weeks without any sensible change or tendency to precipitation. Its taste is bitter and somewhat acid, very different from a mixture of sulphur and water. When boiled, sulphur is precipitated, and sulphuric acid is found in the clear liquid. The milkiness of the liquid seems owing, therefore, to the oxide of sulphur.

T. Thomson regarded the acid component of the liquid as a *sulphosulphurous acid*. M. Cluzel, and W. Schmid showed that the dry gases—hydrogen sulphide and sulphur dioxide—do not react. H. W. F. Wackenroder suspected the presence of pentathionic acid in the products of the action of hydrogen sulphide on an aq. soln. of sulphurous acid. This soln. was afterwards called **Wackenroder's liquid,** although it had previously been prepared by many others—*vide* colloidal sulphur. This liquid was prepared by H. Debus in the following manner :

> A slow current of hydrogen sulphide is passed for 2 hrs., a few degrees above 0°, through 480 c.c. of a nearly sat. soln. of sulphurous acid ; the liquid, still containing a large excess of sulphurous acid, is kept for 48 hrs. in a closed flask at ordinary temp. The operation is repeated ; and continued until all the sulphurous acid is decomposed. This occupies about 2 weeks. If the current of hydrogen sulphide is discontinued as soon as the liquid ceases to smell of sulphurous acid, and the flask removed from the cold water by which it is surrounded, and allowed to stand for a few hours at ordinary temp., it will smell strongly of sulphur dioxide ; the treatment with hydrogen sulphide must then be repeated until, after standing a few hours, the soln. no longer smells of sulphur dioxide. The turbid liquid contains a large precipitate of sulphur which is separated by filtration. The turbid liquid cannot be clarified by filtration through filter-paper. In a bottle of about an inch diameter, it appears semi-transparent ; and of a reddish-brown colour in transmitted light. It becomes more transparent on warming and more opaque on cooling.

A. Sobrero and F. Selmi, and T. Curtius and F. Henkel observed that besides pentathionic acid, the liquid contains tetrathionic, thiosulphuric, and sulphuric acids, but M. J. Fordos and A. Gélis said that these substances are decomposition products of pentathionic acid. V. B. Lewes half neutralized Wackenroder's liquid with barium hydroxide, and obtained a deposit of barium tetrathionate on evaporating the liquid in vacuo; this was followed by a crop of mixed tetrathionate and pentathionate, and finally a crop of the pentathionate crystals alone. Analyses of the ratio of hydrogen to sulphur were found by F. Kessler, T. Takamatsu and W. Smith, and V. B. Lewes to agree with 2 : 5. This does not necessarily establish the existence of pentathionic acid, because the same ratio could be obtained with mixtures of hexathionic acid and trithionic or tetrathionic acid. H. Debus gave for the ratio $H:S:O=2:5:6$. In order to determine the composition of Wackenroder's liquid, H. Debus examined the metal salts which can be obtained from the liquid. He proved that the liquid contains (i) small drops of sulphur in suspension; (ii) sulphur in a colloidal state which he regarded as an allotropic modification—δ-sulphur (*q.v.*); (iii) sulphuric acid; (iv) traces of trithionic acid; (v) tetrathionic acid; (vi) pentathionic acid; and (vii) a polythionic acid with more sulphur than the pentathionic acid—probably hexathionic acid.

H. Debus showed that hydrogen sulphide and sulphur dioxide in the presence of water react with the separation of sulphur. Pentathionic acid is not the direct product of this reaction because the greater part of the pentathionic acid is only slowly formed when a soln. of sulphurous acid partially decomposed by hydrogen sulphide is kept for 3 to 4 hrs. Such a soln. yielded $K_2S_4O_6 : K_2S_5O_6=6:1$ by weight; if treated twice with hydrogen sulphide for $1\frac{1}{2}$ hrs. on separate days, the ratio was 6 : 2; and if treated for 2 hrs. eight times on separate days, 6 : 6. The best yield of pentathionic acid is obtained when the hydrogen sulphide is passed 5 or 6 times with 36–48 hour intervals. The quantity of tetrathionic acid formed is independent of the time of preparation, and it is therefore inferred that tetrathionic acid is a direct product of the action of hydrogen sulphide on sulphurous acid: $3SO_2+H_2S=H_2S_4O_6$. If sulphurous acid, and hydrogen sulphide had no action on tetrathionic acid, this would be the sole product of the reaction; but both these agents decompose tetrathionic acid yielding a complex mixture of products. So long as the sulphurous acid is in great excess, as at the beginning of the operation, most of the hydrogen sulphide reacts with the sulphurous acid, forming tetrathionic acid. The tetrathionic acid slowly reacts with free sulphurous acid, forming trithionic and thiosulphuric acids. The reaction is reversible, and attains a limit. The thiosulphuric acid can then react with tetrathionic acid to form pentathionic acid, so that the liquid now contains sulphurous, thiosulphuric, trithionic, tetrathionic, and pentathionic acids. When hydrogen sulphide is passed into the liquid until all the sulphurous acid is decomposed, the hydrogen sulphide attacks the tetrathionic acid, forming water and sulphur. This sulphur, *in statu nascendi*, converts trithionic into tetrathionic acid: tetrathionic into pentathionic acid; and pentathionic into hexathionic acid. The moment all the sulphurous acid disappears, all the trithionic acid will have been converted into the tetrathionic acid. Another part of the sulphur produced by the action of hydrogen sulphide on tetrathionic acid remains in soln. as colloidal or δ-sulphur, and part separates as a precipitate or suspension. If the hydrogen sulphide is passed through the sulphurous acid with interruptions of several hours' duration, the condensation of thiosulphuric acid to pentathionic acid occurs so that the proportion of pentathionic acid is increased five or six times; and if the passage of hydrogen sulphide be continued after all the sulphurous acid has disappeared, and until it ceases to act on the polythionic acids present, then water and sulphur will be the final products of the decomposition. Any sulphuric acid which may be formed is due to the atmospheric oxidation of sulphurous acid.

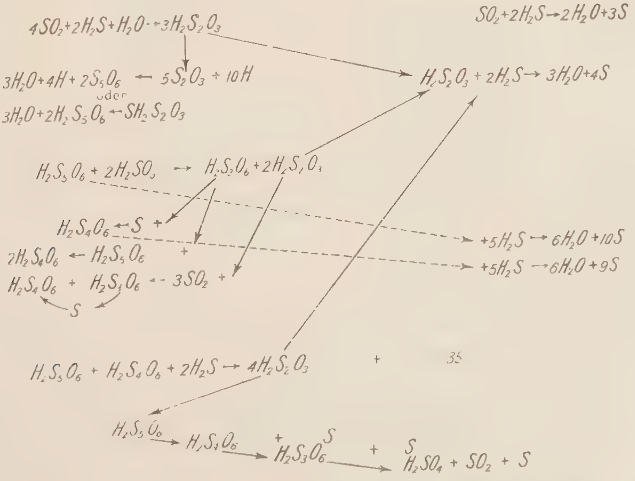
Hence, *H. Debus's theory of the formation of Wackenroder's liquid is that tetrathionic acid is a direct product of the action of hydrogen sulphide on sulphurous acid; and that the other acids are derived from the tetrathionic acid by a series of subsequent* *reactions.* Since a current of hydrogen sulphide ultimately transforms Wackenroder's liquid into sulphur and water, so that the final product of the reaction between hydrogen sulphide and sulphur dioxide can be represented : $2H_2S+SO_2+3S+2H_2O$, the polythionic acids are intermediate products between the original materials—sulphur dioxide, hydrogen sulphide, and water—and the final products—sulphur and water—*vide infra,* trithionic acid, and *vide supra,* thiosulphuric acid.

A number of explanations of the action of hydrogen sulphide on sulphurous acid are based on the formation of intermediate compounds. H. Bassett and R. G. Durrant represented the first stage of the reaction between sulphurous acid and hydrogen sulphide by $H_2S+H_2S_2O_5\rightleftharpoons HO.S.O.S.OH+S(OH)_2$. Hence, sulphoxylic acid and its pyroderivative represent the first products of the reaction. The sulphoxylic acid reacts with hydrogen sulphide to form sulphur : $S(OH)_2+H_2S\rightleftharpoons 2H_2O+2S$; and the freshly-formed sulphur is in a favourable condition for reacting with sulphurous acid to form thiosulphuric acid : $S+H_2SO_3\rightleftharpoons H_2S_2O_3$, which is relatively stable in dil., feebly acid soln. Trithionic acid is formed from the thiosulphuric acid : $2H_2S_2O_3\rightleftharpoons H_2S+H_2S_3O_6$, and some trithionate may be formed from sulphurous and sulphoxylic acids : $2S(OH)_2+H.HSO_3=H_2O+HO.SO_2.S.SO_2.OH$. F. Förster and R. Vogel suggested the reaction : $SO+2HSO_3'=S_3O_6''+H_2O$ for the trithionate formation. H. Bassett and R. G. Durrant found that traces of polythionates are produced by shaking sulphurous acid with a soln. of sulphur in benzene ; and by passing sulphur dioxide and sulphur vapour simultaneously into water a soln. containing $0{\cdot}32N$-H_2SO_3, and $0{\cdot}01N$- with respect to a mixture of trithionic and tetrathionic acid was obtained. F. Förster and K. Centner also conclude that some trithionate is formed directly : $S_2O_3''+4HSO_3'+2H^{\cdot}=2S_3O_6''+3H_2O$, and not by the degradation of pentathionic acid. The hypothesis of H. Bassett and R. G. Durrant can be adapted to explain the results of H. Debus, and of E. H. Riesenfeld and G. W. Feld, as well as the hypothesis based on the primary formation of sulphoxylic acid : $H_2SO_3+H_2S\rightleftharpoons H_2SO_2+H_2SO$; or the hypothesis of E. H. Riesenfeld and G. W. Feld based on the primary reaction : $H_2S+2H_2SO_3=3(HO)_2S(\text{or } SO+H_2O)$; or the hypothesis of F. Förster and A. Hornig based on the primary reaction : $H_2S+H_2SO_3\rightleftharpoons H_2S_2O_2+H_2O$. No proof of the primary formation of sulphoxylic acid is possible other than the bleaching of indigo, or methylene-blue by sulphurous acid freshly treated with hydrogen sulphide. The bleaching of indigo by these soln. was first observed by W. Spring. The test is ambiguous for the bleaching also occurs with hyposulphurous acid. F. Rashig, E. H. Riesenfeld and G. W. Feld, F. Förster and co-workers, and A. Kurtenacker and M. Kaufmann have suggested hypotheses in which pentathionic acid is the first formed thionic acid. According to H. Bassett and R. G. Durrant's hypothesis, the first thionic acid to appear during the decomposition of thiosulphate is trithionic acid, and this is usually accompanied by some tetrathionic acid, and in a very short time by some pentathionic acid. Pentathionic acid is the last thionic acid to be formed, trithionic acid the first. When hydrogen sulphide and sulphurous acid react in dil. soln., trithionic acid is the first thionic acid to appear, and tetrathionic and pentathionic acids are built up from trithionic acid by the assimilation of sulphur : $H_2S_3O_6+S=H_2S_4O_6$; and $H_2S_4O_6+S=H_2S_5O_6$.

As just indicated, E. Heinze supposed that sulphoxylic acid, H_2SO_2, the acid of the anhydride SO, and the acid H_2SO of the anhydride S_2O, is first formed. He said that when aq. soln. of sulphur dioxide and hydrogen sulphide interact, the former behaves like sulphurous acid not sulphur dioxide, and sets up the reversible primary reaction : $H_2SO_3+H_2S\rightleftharpoons H_2SO_2+H_2SO$, and the precipitation of sulphur is caused by the decomposition of the compound H_2SO, which is assumed to be of the hydrogen dioxide type. This compound is also supposed to be formed by the further action of hydrogen sulphide on the sulphoxylic acid, thus : $H_2SO_2+H_2S\rightleftharpoons 2H_2SO$. Consequently, the final result of the interaction of one mol. of sulphurous acid with two mols. of hydrogen sulphide is given by the equation

$2H_2S+SO_2=3S+2H_2O$. The reaction is completed, however, only after several months. The final state is reached more quickly in presence of an excess of hydrogen sulphide. Hydrogen sulphide also reacts with polythionic acids to form sulphur and water. When excess of sulphurous acid is present, less sulphur is precipitated and more polythionic acid formed. After about a day, a condition of equilibrium obtains. If, now, the precipitated sulphur is filtered off and the excess of sulphur dioxide removed by a current of nitrogen, in a short time more sulphur comes down and sulphur dioxide again appears in the soln. The sulphur, when once precipitated, takes no further part in the process, and the reversible reactions are supposed to involve the polythionic acids, sulphurous acid, and the compounds H_2SO_2 and H_2SO, thus: (i) $H_2SO_2+SO_2 \rightleftharpoons H_2S_2O_4$; (ii) $H_2SO+H_2SO_3 \rightleftharpoons H_2S_2O_3+H_2O$; (iii) $H_2S_2O_4+H_2S_2O_3 \rightleftharpoons H_2S_4O_6+H_2O$; (iv) $H_2S_4O_6+H_2S_2O_3 \rightleftharpoons H_2S_5O_6+H_2SO_3$. With increasing conc. of sulphur dioxide, the proportion of tetrathionic acid increases, whilst that of pentathionic acid decreases. This is attributed to the dehydration of the sulphurous acid owing to the increasing acidity of the soln., with consequent increase in the production of $H_2S_2O_4$ by equation (i). When soln. containing an excess of sulphur dioxide are allowed to remain for several weeks, increasing quantities of sulphuric acid are formed. Possibly, it is due to the decomposition of trithionic acid, which may be formed in small quantities and is known to decompose into sulphuric acid, sulphur dioxide, and free sulphur. E. H. Riesenfeld and G. W. Feld found that at 0°, the optimum ratio for polythionate formation was $2SO_2 : H_2S$, and with the ratio $SO_2 : 2H_2S$, all the sulphur was precipitated in the elementary form. Immediately after the preparation of the soln. $2SO_2 : H_2S$, there is evidence of the formation of an intermediate compound which can be precipitated at a low temp. as the barium salt; in soln., the intermediate compound changes to thiosulphate. The proportion of tri- and tetra-thionic acids formed after 14 days depends on the conc. of the sulphur dioxide. A low concentration of sulphur dioxide favours the tetrathionate. The proportion of pentathionate is practically constant. This does not agree with E. Heinze's conclusions. The sulphuric acid which is always formed reaches a maximum near the commencement of the reaction; it must therefore be formed from the intermediate compound, not by oxidation of the polythionic acids. Of the three polythionic acids, the tetrathionic acid is the least stable and decomposes relatively quickly into tri- and penta-thionic acids. The trithionic acid decomposes more slowly with formation of sulphur dioxide, whilst pentathionic acid decomposes only in the course of months with separation of sulphur. The order of stability is the same in neutral as in acid soln.; in alkaline soln., all the polythionates decompose quickly into thiosulphate and sulphite. The phenomena observed are explained on the assumption that the intermediate compound is a hydrate of the unknown **sulphur monoxide,** SO. This is stable in acid soln. for a time, but in neutral or alkaline soln. quickly forms thiosulphate. In acid soln., it slowly polymerizes to pentathionic acid. By combination with sulphurous acid it forms tri- and tetra-thionic acids: $3SO+H_2SO_3=H_2S_4O_6$; $SO+2SO_2+H_2O=H_2S_3O_6$. By hydrogen sulphide, it is reduced to sulphur. F. Förster assumed that in aq. soln. there is a state of equilibrium between sulphoxylic acid and its hypothetical anhydride, $H_2SO \rightleftharpoons SO+H_2O$; and that the other sulphur acids are formed by reactions: (i) $SO+H_2S=2S+H_2O$; (ii) $2SO+H_2O=S_2O_3''+2H^{\cdot}$; (iii) $SO+2HSO_3'=S_2O_6''+H_2O$; and (iv) $SO+2HS_2O_3'=S_5O_6''+H_2O$. He also assumed that the initial reactions in the formation of Wackenroder's soln. involve $H_2S+H_2SO_3=S_2(OH)_2+H_2O$, followed by $S_2(OH)_2+H_2SO_3+H_2O \rightleftharpoons 3H_2SO_2$, and $S_2(OH)_2+H_2S \rightleftharpoons 2H_2O+3S$. Equation (iii) is preferred to that suggested by H. Bassett and R. G. Durrant for the formation of trithionic acid. F. Förster and E. T. Mommsen, and F. Förster and A. Hornig represented the reaction between sulphurous acid and hydrogen sulphide as a balanced process involving the intermediate formation of the hypothetical $H_2S_2O_2$, thus: $H_2S+H_2SO_3 \rightleftharpoons H_2S_2O_2+H_2O$; but a further reaction with hydrogen sulphide produces sulphur, while an excess of sulphurous acid produces pentathionic acid. They added that the trithionates are least stable, the tetrathionates the most stable. None of the polythionic acids is stable in aq. soln., and the following decompositions occur in soln.: $S_5O_6'' \rightleftharpoons S_4O_6''+S$; $S_4O_6'' \rightleftharpoons S_3O_6''+S$; $S_3O_6''+H_2O=SO_4''+S_2O_3''+2H^{\cdot}$; $S_2O_3''+H^{\cdot} \rightleftharpoons HSO_3'+S$. The insolubility of sulphur removes it from the equilibrium, and at boiling temp. the sulphur dioxide is removed and SO_4'' is alone left in soln.; side reactions were also found to take place. The more sulphur dioxide and sulphur there remains in the soln., the greater is the tendency of thiosulphuric acid to polymerize, *e.g.* $S_3O_6''+S_2O_3''+H^{\cdot} \rightleftharpoons S_4O_6''+HSO_3'$; $S_4O_6''+S_2O_3''+H^{\cdot} \rightleftharpoons S_5O_6''+HSO_3'$. A high conc. of hydrogen-ion retards the decomposition of tetra- and penta-thionic acids, but not of trithionic acid. F. Förster also said that in addition to the formation of thiosulphate: $2SO+H_2O \rightleftharpoons S_2O_3''+2H^{\cdot}$, the intermediate product, sulphur monoxide, may produce polythionic acids by other changes, *e.g.* $SO+2S_2O_3''+2H^{\cdot}=S_5O_6''+H_2O$; and $SO+2HSO_3'=S_3O_6''+H_2O$, analogous to what is known in the case of selenium monoxide. For the development of thiosulphates, *vide* sodium thiosulphates. E. Josephy said that tetrathionic acid is a direct product of the reaction: $3SO_2+H_2S=H_2S_4O_6$, whilst the sulphur formed in the reaction: $SO_2+2H_2S=3S+2H_2O$, also reacts with sulphur dioxide: $5S+5SO_2+2H_2O=2H_2S_5O_6$. Pentathionic acid can also be formed by the action of the sulphur and sulphur dioxide produced when a thiosulphate is treated with an acid. These reactions, added E. Josephy, explain all the cases of polythionate formation without assuming hypothetical intermediate products. The case of the intermediate compound was defended by E. H. Riesenfeld, and F. Förster; F. Raschig, likewise, supposed that in the formation of pentathionic acid from hydrogen sulphide and sulphurous acid, $SO_2+H_2S=SO+S+H_2O$, five SO-groups condense with the addition of water. The alternative reaction $H_2S+2SO_2=3SO+H_2O$ is excluded; while if hydrogen sulphide is in excess, the reaction proceeds smoothly: $2H_2S+SO_2=3S+2H_2O$. Hyposulphurous acid is not formed.

W. R. Lang and C. M. Carson showed that if very little moisture be present, the two gases—hydrogen sulphide and sulphur dioxide—react to form sulphur and water: $2H_2S+SO_2=3S+2H_2O$. The sulphur, water, and sulphurous acid then react to form polythionic acids. This subject is further discussed in connection with the action of hydrogen sulphide (*q.v.*) on sulphurous acid. W. Petzold summarized his ideas of the interrelations of the polythionic acids in Wackenroder's soln. by the scheme:


$4SO_2+2H_2S+H_2O \rightarrow 3H_2S_2O_3$
$SO_2+2H_2S \rightarrow 2H_2O+3S$
$3H_2O+4H+2S_5O_6 \leftarrow 5S_2O_3+10H$
oder
$3H_2O+2H_2S_5O_6 \leftarrow 5H_2S_2O_3$
$H_2S_2O_3+2H_2S \rightarrow 3H_2O+4S$
$H_2S_5O_6+2H_2SO_3 \rightarrow H_2S_5O_6+2H_2S_2O_3$
$H_2S_4O_6 \leftarrow S$ +
$2H_2S_4O_6 \leftarrow H_2S_5O_6$ +
$H_2S_4O_6 + H_2S_3O_6 \leftarrow 3SO_2$ +
S
$+5H_2S \rightarrow 6H_2O+10S$
$+5H_2S \rightarrow 6H_2O+9S$
$H_2S_5O_6+H_2S_4O_6+2H_2S \rightarrow 4H_2S_2O_3$ + 3S
$H_2S_5O_6 \rightarrow H_2S_4O_6$ + S $\rightarrow H_2S_3O_6$ + S $\rightarrow H_2SO_4+SO_2+S$

H. Debus described Wackenroder's liquid as a milky fluid which may be kept for weeks without becoming clear. A drop under the microscope appears to be homogeneous, but after 5 mins., a ring of yellow particles appears on the edges and grows towards the centre of the drop. The deposit is composed of minute drops of sulphur; and is greater than the amount of sulphur in suspension. Hence, it is produced by the precipitation of dissolved sulphur. The addition of a little water causes this sulphur to dissolve. Carbon disulphide, benzene, ether, olive oil, chloroform, or tannin do not clear the liquid, but powder of charcoal, barium carbonate, alkalies, a conc. soln. of hydrochloric acid, nitric acid, and potassium nitrate cause complete precipitation of the sulphur in suspension and soln. The addition of much water causes the emulsion to become almost clear; at least, in layers of an inch in thickness, it appears perfectly clear, transparent, and slightly yellow. Soln. of saltpetre produced in this dil., clear liquid a copious precipitate of sulphur. The drops of sulphur in suspension in the emulsion appear, therefore, to be soluble in much water. Wackenroder's soln. can be concentrated on a water-bath without decomposition until it reaches a sp. gr. 1·32. The δ-sulphur is all coagulated before it reaches this point of conc. Further evaporation on the water-bath causes evolution of sulphurous acid and precipitation of sulphur. Under reduced press., over pieces of potassium hydroxide, the liquid can be concentrated to a sp. gr. 1·46. This liquid is regarded by H. W. F. Wackenroder, F. Kessler, T. Takamatsu and W. Smith, and V. B. Lewes as pentathionic acid. W. Spring regarded it as a soln. of sulphur in tetrathionic acid. H. Debus added that Wackenroder's liquid of the sp. gr. 1·46, is a colourless, transparent, oily liquid of great refractive power and intensely acid. It destroys the coherence of the fibres of filtering-paper, and can only be filtered when of sp. gr. lower than 1·4. A sample of sp. gr. 1·3 was kept in a dark place for 3 months without apparent change; a slow decomposition then occurred with the evolution of sulphur dioxide and the separation of sulphur. The decomposition was not completed in two years. The potassium salts or the acids in Wackenroder's liquid decompose into trithionic acid with the separation of sulphur: $H_2S_5O_6=H_2S_4O_6+S$; $2H_2S_4O_6=H_2S_5O_6+H_2S_3O_6$; and the trithionic acid decomposes into sulphuric acid, sulphur dioxide and sulphur: $H_2S_3O_6=H_2SO_4+SO_2+S$. The liberated sulphur, however, recombines with the undecomposed trithionic acid re-forming tetrathionic acid: $H_2S_3O_6+S=H_2S_4O_6$, or pentathionic acid: $H_2S_3O_6+2S=H_2S_5O_6$. The reactions are reversible, taking place in opposite directions with equal facility. This behaviour, said H. Debus, is connected with their heats of formation since J. Thomsen found that:

	Cals.	Difference.
Dithionic acid, $(S_2,O_6,Aq.)$	211·08	—
Trithionic acid, $(S_3,O_6,Aq.)$	201·76	9·32
Tetrathionic, $(S_4,O_6,Aq.)$	192·43	9·32
Pentathionic acid, $(S_5,O_6,Aq.)$	183·11	9·32

This shows that the different sulphur atoms are of equal thermochemical value. According to M. Berthelot, the heat developed per atom of oxygen is practically constant, meaning that the combination of oxygen with sulphur develops practically the same quantity of heat whatever be the degree of condensation of the sulphur. M. Berthelot found that the heats of formation are:

	Cals.
Dithionic acid $(2S,O_5,H_2O,Aq.)$	206·8
Trithionic acid $(3S,O_5,H_2O,Aq.)$	211·4
Tetrathionic acid $(4S,O_5,H_2O,Aq.)$	205·2
Pentathionic acid $(5S,O_5,H_2O,Aq.)$	215·8

H. Debus said that J. Thomsen's data show that the heat developed during the formation of the polythionic acids from water and the elements become less and less as the acids become richer in sulphur. When trithionic acid unites with an atom of sulphur 9·33 Cals. are rendered latent, and the same quantity of energy is rendered latent when tetrathionic acid unites with an atom of sulphur to form pentathionic acid, so that the compounds are endothermic with regard to these sulphur atoms. A sulphur atom which detaches itself from a mol of tetrathionic acid carries away an amount of energy corresponding with about 9·33 Cals., and this amount is sufficient to enable the atom to reunite with a mol of trithionic acid to form tetrathionic acid, or with the latter to form pentathionic acid. Like a pendulum which during its fall acquires the necessary *vis viva* to rise again to a height equal to that of its descent, so the sulphur atoms of one polythionic acid acquire during their separation the necessary energy to combine with another polythionate. In a soln. of tri-, tetra-, and penta-thionic acids, decomposition and re-formations are continuously going on so that the sulphur atoms are in uninterrupted migration from acid to acid. If the state of equilibrium between the decomposition and formation of the polythionic acids could be maintained, their relative proportions in soln. would remain unaltered; but this is prevented by the decomposition of the trithionic acid to sulphuric and sulphurous acids and sulphur. This chemical change is not reversible. The oxidation of sulphurous acid to sulphuric acid also exercises a disturbing influence by hindering the decomposition of pentathionic and tetrathionic acids. As soon as the sulphuric acid has accumulated to a certain concentration, the decomposition of the penta- and tetra-thionic acids will cease, but that of the trithionic acid will continue. Hence, the final state of equilibrium, after a long time, would be a liquid containing sulphuric, tetrathionic, and pentathionic acids, and sulphur, each of a certain definite concentration, and not undergoing a further chemical change.

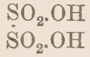
H. Hertlein found that the mol. vol. of the potassium polythionates increases regularly from the di- to the tetra-thionates; the viscosity of the soln. increases with an increase in the sulphur content; the mol. refraction of the soln. also increases in a similar way, and the results indicate that all the sulphur is present in the bivalent form; the electrical conductivities were also measured; and the relative ionic velocities were found to be $\frac{1}{2}S_2O_6$, 85; $\frac{1}{2}S_3O_6$, 72·8; $\frac{1}{2}S_4O_6$, 67·4; and $\frac{1}{2}S_5O_6$, 61·4. The percentage degrees of ionization for a mol of the dithionic and tetrathionic acids dissolved in 42·18 litres of water are respectively 89·6 and 92·0. The e.m.f. of a mercury electrode in contact with soln. of the polythionates against a normal cathode decreased with an increasing content of sulphur in the molecule. E. Josephy, and F. Förster and A. Hornig found trithionic acid to be the least

TABLE XVII.—SOME REACTIONS OF THE POLYTHIONIC ACIDS.

Solution.	Dithionates.	Trithionates.	Tetrathionates.	Pentathionates.
KOH	No pp.	No pp.	No pp.	Pp. of sulphur
Dil. HCl	Nil	Evolution SO_2; pp.	Nil	Nil
$HgNO_3$	No. pp.	Black pp. becomes white on standing	Yellow pp. gradually darkens	Yellow pp. white on standing with excess H_3NO_3
$AgNO_3$	No pp.	Yellow pp. soon blackens	Yellow pp. soon blackens; also blackened NH_3	Yellow pp., gradually darkens; blackened by NH_3
$AgNO_3$ (ammoniacal)	—	No brown coloration on standing when warmed Ag_2S pp.	No brown colour even on standing unless warmed	Almost immediate brown coloration; blackens on warming
$HgCy_2$	No pp.	Yellow precipitate blackens slowly.	Yellow pp., blackens on warming, evolves HCy	Yellow pp., blackens on warming, evolves HCy
$HgCl_2$	No pp.	Yellow pp. whitens with excess $HgCl_2$	White pp. on warming	Whitish-yellow pp. on warming
KHS	—	—	White pp. of S	White pp. of S
Dil. $KMnO_4$	One drop immediate brown pp.	One drop immediate brown pp. even in presence of dil. H_2SO_4	Decolorized without adding dil. H_2SO_4; no pp.	Decolorized without adding dil. H_2SO_4; no pp.

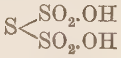
stable and tetrathionic acid the most stable of these acids. They decompose $S_5O_6'' \rightleftharpoons S_4O_6''+S$; $S_4O_6'' \rightleftharpoons S_3O_6+S$; $S_3O_6'' \rightleftharpoons SO_4''+SO_2+S$, or $S_3O_6''+H_2O = SO_4''+S_2O_3''+2H\cdot$ and $S_2O_3''+H\cdot = HSO_3'+S$. A. Casolari found that a polythionate containing n-atoms of sulphur in the molecule yields $n-1$ mols. of sulphuric acid when treated with hydrogen dioxide: $Na_2SO_6+(3n-5)H_2O_2 +(n-1)H_2O = Na_2SO_4+(n-1)H_2SO_4+(3n-5)H_2O$. If the soln. be quite neutral, the acid can be determined by titration with standard alkali. According to H. Debus, mercurous nitrate gives a yellow precipitate with penta- and tetra-thionate soln., and a black precipitate with trithionate soln.; copper sulphate gives no reaction in the cold, but gives a black precipitate with trithionate in boiling soln.; barium chloride gives no precipitate with soln. of any of the polythionates; mercury cyanide forms mercuric sulphide and sulphuric acid: $HgCy_2+H_2S_4O_6=2HCy+HgS_4O_6$; and $HgS_4O_6+2H_2O=HgS+S+2H_2SO_4$; $HgCy_2+H_2S_5O_6+2H_2O=2H_2SO_4+2S+HgS+2HCy$. According to A. Longi and L. Bonavia, potassium permanganate, in alkaline soln., oxidizes potassium sulphite, thiosulphate, trithionate, tetrathionate, sulphide, and polysulphide to potassium sulphate; potassium dithionate is not oxidized at all, and the oxidation of the tri- or tetra-thionate proceeds slowly. Sodium dioxide immediately and completely oxidizes sulphites, thiosulphates, trithionates, tetrathionates, sulphides, and polysulphides, but acts very slowly on the dithionates. Some typical reactions of the polythionic acids, summarized mainly by T. Takamatsu and W. Smith, are given in Table XVII. According to J. J. P. Valeton, these reactions of pentathionic acid are given also by hydrosols of sulphur.

The constitution of the polythionic acids.—C. W. Blomstrand, and D. I. Mendeléeff based a theory of the constitution of the polythionic acids on the type theory —**1**. 5, 16—in which the univalent radicle SO_2OH, or HSO_3, replaces the radicles of hydrogen, hydrogen sulphide, or the hydrogen polysulphides. The sulphonic radicle $SO_2.OH$ thus corresponds with the carboxylic radicle CO.OH of organic chemistry. Thus, replacing one hydrogen atom in the hydrogen molecule by the HSO_3-radicle furnishes sulphurous acid $H.HSO_3$; and replacing both hydrogen atoms by this radicle yields dithionic acid, $HSO_3.HSO_3$; replacing a hydrogen atom in hydrogen sulphide by HSO_3 yields thiosulphuric acid, $HS.HSO_3$, and replacing both hydrogen atoms in a similar way furnishes trithionic acid, $HSO_3.S.HSO_3$, replacing both hydrogen atoms of hydrogen disulphide by the HSO_3 radicle yields tetrathionic acid, $HSO_3.S.S.HSO_3$; and proceeding similarly with hydrogen trisulphide there is obtained pentathionic acid, $HSO_3.S.S.S.HSO_3$. The acids are thus formulated:



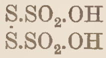
$$\begin{array}{l} SO_2.OH \\ SO_2.OH \end{array}$$

Dithionic acid.



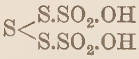
$$S\begin{array}{l} \diagup SO_2.OH \\ \diagdown SO_2.OH \end{array}$$

Trithionic acid.



$$\begin{array}{l} S.SO_2.OH \\ S.SO_2.OH \end{array}$$

Tetrathionic acid.



$$S\begin{array}{l} \diagup S.SO_2.OH \\ \diagdown S.SO_2.OH \end{array}$$

Pentathionic acid.

The analogous thiosulphuric acids are unknown. This hypothesis is supported by the experiments of W. Spring in which a trithionate was produced by the action of sulphur dichloride on a neutral sulphite: $SCl_2+2(K.SO_2OK)=2KCl +S(SO_2.OK)_2$; similarly, sulphur monochloride also yields a trithionate mixed with some thiosulphate, and not the tetrathionate as was anticipated by D. I. Mendeléeff: $S_2Cl_2+2(K.SO_2.OK)=S_2(SO_2.OK)_2+2KCl$. W. Spring, however, used water in his experiments; and H. Debus pointed out that the sulphur dichloride then decomposes into sulphurous and hydrochloric acids and sulphur. If the concentrations of the reacting substances are such that the hydrochloric acid produced decomposes half the potassium sulphite into potassium chloride, water, and sulphurous acid, the potassium sulphite and sulphur will form potassium thiosulphate which, reacting with the sulphurous acid, produces trithionate. The synthesis of these acids by the iodine reactions, and their decomposition by sodium also support this hypothesis, but the argument is not decisive because the results admit of several interpretations —*vide infra*. H. Baubigny said that the formation of dithionates by heating silver sulphite or sodium silver sulphite shows that dithionic has two sulphonic radicles. P. Pascal's magnetic observations favoured $HO.SO_2.OH$ for dithionic acid, and $HO.SO_2.S_n.SO_2.OH$ for the polythionic acids; and likewise A. Colefax supported the chain formula from his observations on the removal of sulphur from the tetrathionate by a sulphite so as to form a trithionate and thiosulphate. F. Calzolari, and T. S. Price and D. F. Twiss emphasized the relationship of the tetrathionates $HO.SO_2.S.S.SO_2.OH$ and the persulphates $HO.SO_2.O.O.SO_2.OH$. J. von Szilagyi said that the trisulphide formula for trithionic acid is supported by the formation of that acid by the decomposition of potassium arsenothiosulphate:

$$(KO.SO_2.\boxed{S)_3As+As}(S.SO_2.OK)_3=As_2S_3+3(KO.SO_2.S.SO_2.OK).$$

C. W. Blomstrand, and D. I. Mendeléeff's mode of viewing the constitution of the polythionic acid favours the asymmetric formulæ for the sulphites and thiosulphates (*q.v.*). A. Michaelis based formulæ for dithionic and trithionic acids on the symmetrical formula of sulphurous acid, $SO(OH)_2$, and formulæ for tetrathionic and pentathionic acids, on the asymmetrical formula of thiosulphuric acid, $HO.SO_2.SH$. This hypothesis furnishes:

$$\begin{array}{cccc}
\begin{matrix}HO.SO.O\\ HO.SO.\dot{O}\end{matrix} & \begin{matrix}HO.SO.O\\ HO.SO.O\end{matrix}\!>\!S & \begin{matrix}HO.SO.O.\dot{S}\\ HO.SO.O.S\end{matrix} & \begin{matrix}HO.SO.O.S\\ HO.SO.O.S\end{matrix}\!>\!S \\
\text{Dithionic acid.} & \text{Trithionic acid.} & \text{Tetrathionic acid.} & \text{Pentathionic acid.}
\end{array}$$

According to M. Berthelot, the thionic acids may be regarded as derivatives of condensed simple or mixed anhydrides, which are themselves derived from thiosulphuric and sulphurous anhydrides. Thus, thiosulphuric acid is derived from the anhydride S_2O_2 by the action of water $S_2O_2+H_2O=H_2S_2O_3$. This can give rise to a series of condensed anhydrides, $nS_2O_2.(n-m)H_2O$, where the basicity of the resulting acids is proportional to m. Thus, when $n=5$ and $m=3$, pentathionic acid, $5S_2O_3.2H_2O$, or $2H_2S_5O_6$, is formed; when sulphurous acid, $SO_2.H_2O$, is present it may behave in a similar way, and the mixed condensed anhydrides, $4S_2O_2.SO_2.H_2O$, is tetrathionic acid; $S_2O_2.4SO_2.2H_2O$ is trithionic acid; and $4S_2O_2.SO_2.2H_2O$ is said to be the acid obtained in the first crystallizations when preparing pentathionic acid by H. Debus' method. This is said to be supported by the behaviour of the thionic acids with an excess of alkali hydroxide.

H. Debus started from the asymmetrical formula of the sulphites, $H.SO_2.OH$, and the assumption that the sulphur of the polythionates enters the molecule *viâ* the $H.SO_2$-complex, forming $HS_2.SO_2$-, and $HS.S.SO_2$-radicles. A molecule of potassium sulphide can combine with 2, 3, or more atoms of sulphur to form a series of polysulphides, and this property is not lost in the combination $K.SO_2$-radicle. Hydrogen sulphide also takes up more sulphur, forming the polysulphides. This association of sulphur occurring with the sulphides and the thionic acids confirms similar properties on the compounds in which they occur. Tetrathionic acid contains the radicles HS, and HO, and pentathionic acid, the radicles HS_2 and HO. Thus,

$$\begin{array}{cccc}
\begin{matrix}H.SO_2.O\\ HO.SO_2.\dot{S}\end{matrix} & \begin{matrix}HS.SO_2.O\\ HO.SO_2.\dot{S}\end{matrix} & \begin{matrix}HS.S.SO_2.O\\ HO.SO_2.\dot{S}\end{matrix} & \begin{matrix}HS.S.S.SO_2.O\\ HO.SO_2.\dot{S}\end{matrix} \\
\text{Trithionic acid.} & \text{Tetrathionic acid.} & \text{Pentathionic acid.} & \text{Hexathionic acid.}
\end{array}$$

H. Debus quoted the following facts in support of his hypothesis. The formation of potassium tetrathionate from potassium thiosulphate and iodine might be quoted in support of any one of the formulæ: $KO.SO_2.S.S.SO_2K$; $KS.SO_2.O.O.SO_2SK$; or $KS.SO_2.O.S.SO_2.OK$. The loss of an atom of sulphur by the tetrathionate would give respectively the formulæ $S(SO_2.OK)_2$; $K.SO_2.O.O.SO_2.SK$; or $K.SO_2O.S.SO_2.OK$. Potassium trithionate, like potassium sulphite, can take up an atom of sulphur *in statu nascendi*, and this is taken by H. Debus to mean that both contain the same radicle $K.SO_2$. This is supported by the formation of the trithionate from potassium hydrosulphite and sulphur. This does not favour the formula $S(SO_2.OK)_2$ for the trithionate. If an atom of sulphur is removed from the trithionate, it decomposes into sulphate and sulphurous acid, and from these materials the original salt cannot be obtained by direct combination. Hence, the existence of the polythionate is dependent on the one sulphur atom. This favours the formula $K.SO_2.O.S.SO_2.OK$, but not $K.SO_2.O.O.SO_2.SK$. H. Debus continued, if potassium pentathionate has the constitution $S_3(SO_2.OK)_2$, it might be anticipated that bromine would react: $S_3(SO_2.OK)_2+Br_2+2H_2O=3S+2KBr+2H_2SO_4$; actually, the reaction proceeds more in accord with $2K_2S_5O_6+8Br_2+15H_2O=4KBr+4S+6H_2SO_4+12HBr$, and if less bromine is used, a proportionate quantity of pentathionate remains undecomposed; two atoms of the sulphur of a mol. of potassium pentathionate, $K_2S_5O_6$, are precipitated as such, and three are oxidized to sulphuric acid. The conclusion is that the three oxidizable atoms of sulphur are already in the mol of pentathionate in combination with oxygen, and are so in the trithionate resulting from the decomposition of the pentathionate. According to K. Jellinek, and I. M. Kolthoff, the oxy-acids of sulphur can be arranged in the order of increasing strength in the series: H_2SO_3, $H_2S_2O_4$, $H_2S_2O_3$, H_2SO_4, $H_2S_2O_6$, and $H_2S_3O_6$, so that dithionic and trithionic acids are of about the same strength, and so are thiosulphuric and sulphuric acids, whilst sulphurous acid is the weakest of the series, and hydrogen sulphide is weaker still. The relative stabilities of the polythionic acids have been discussed by E. H. Riesenfeld and G. W. Feld, and F. Förster and A. Hornig. I. Vogel said that in accord with the thermal data of F. Martin and L. Metz, the stabilities should decrease in the order dithionic, trithionic, tetrathionic, and pentathionic acid, since the heats of formation, *Q* Cals., are:

	$K_2S_2O_6$	$K_2S_3O_6$	$K_2S_4O_6$	$K_2S_5O_6$	K_2SO_3	$K_2S_2O_3$
Q . .	415	401	393	386	273	283

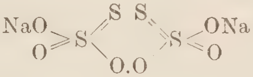
H. Bassett and R. G. Durrant, however, added that this statement can have a definite meaning only when referred to specified conditions. They added that the proportions of tri, tetra-, and penta-thionic acids which can exist in a soln. depend, among other things, upon the hydrogen-ion concentration, increase and decrease of which favour the formation of penta- and tri-thionic acid, respectively. The effect of change of acidity is so great that the separation of sulphur on addition of alkali is almost as delicate a test for pentathionate as is the ammoniacal silver nitrate test. H. Hertlein found that the sp. refractivities of the potassium salts differed by about 15 units per atom of sulphur. This corresponds with the refractivity of bivalent sulphur, and it was therefore assumed that the polythionate sulphur atom is bivalent. He argued that when a metal is directly attached to a sulphur atom there is a great tendency to form complex ions with mercury or silver salts, and this can be detected by e.m.f. measurements. Thus, the e.m.f. of the combination $Ag|0.0022N\text{-}AgNO_3$ against a standard calomel cell is -0.92 volt, and when $0.5N\text{-}K_2S_2O_3$ is added, and the complex salt $KAgS_2O_3$ formed—complex ion AgS_2O_3'—the e.m.f. rose to -0.23 volt. At a dilution of 20 litres, the e.m.ff. were:

	$K_2S_2O_6$	$K_2S_3O_6$	$K_2S_4O_6$	$K_2S_5O_6$
E.m.f. .	0·90	0·79	0·89	0·88

The slight change in the e.m.f. here observed indicates that no complex ion is formed, and that the metal is not therefore directly attached to sulphur as in H. Debus' formula. Consequently, H. Hertlein said that the hypothesis of D. I. Mendeléeff on the constitution of the polythionates harmonizes better with the ionic theory than is the case with H. Debus' hypothesis—*vide supra*, the thiosulphates.

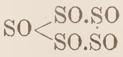
I. Vogel showed that the chain formulæ do not give a rational explanation of the gradual increase with time of the relative quantities of tetrathionates and pentathionates in the products of the interaction of sulphur sesquioxide with water, etc., of the exclusive formation of trithionate in the reaction between a conc. soln. of potassium acetate and a soln. of sulphur sesquioxide in oleum (I. Vogel and J. R. Partington); the liberation of *two* atoms of sulphur from pentathionates by bromine and by mercuric cyanide (H. Debus), and by mercuric chloride (A. Sander, and E. H. Riesenfeld and G. W. Feld); the separation of *one* atom of sulphur from pentathionates by treatment with a cold soln. of sodium carbonate (F. Raschig); the conversion of tetrathionates into pentathionates by acidified soln. of sodium thiosulphate, and the formation of dithionates by the action of acid soln. of potassium permanganate on trithionates (F. Raschig); the strong acidity of the polythionic acids, and the non-formation of complex ions with mercury and silver salts (H. Hertlein); and the difference in the refractivity corresponding with bivalent sulphur between two consecutive polythionates—*e.g.* $K_2S_4O_6$ and $K_2S_5O_6$ (H. Hertlein).

While C. W. Blomstrand, and D. I. Mendeléeff assigned the formula of the polythionates to the persulphidic type—*e.g.* $HSO_3.S.S.HSO_3$, derived from $NaO.SO_2.SNa$ for sodium thiosulphate—A. Gutmann preferred the peroxidic type—*e.g.* $HS_2O_2.O.O.HS_2O_2$, or



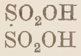
derived from $S : S(ONa)_2 : O$ for sodium thiosulphate. Perdisulphuric acid readily loses oxygen—*i.e.* it is an oxidizing agent; tetrathionic acid readily loses sulphur—*e.g.* it is a sulphurizing agent, for it converts a sulphite into a thiosulphate, and a cyanide into a thiocyanate. A. Gutmann said that the reaction of tetrathionate with sodium arsenite in alkaline soln., forming two mols of monosulphoarsenate, one mol of arsenate, and two mols of sulphite, can be symbolized in skeletal form: $S_4O_5=2S+O+2SO_2$; hence, the withdrawal of two atoms of sulphur from a mol of tetrathionate would form residues which, uniting in pairs, would give a dithionate if the structure is of the perdisulphidic type, and this would not give arsenate and sulphite because dithionates do not react with arsenites. T. S. Price and D. F. Twiss, however, showed that it is more likely that the two $NaSO_3'$-residues would react: $2NaSO_3'+2NaOH=2Na_2SO_3+H_2O+O$; and similar explanations would apply to sodium trithionate, and to the action of potassium cyanide on the tetrathionate. Hence, A. Gutmann's argument against the persulphidic formula has but little weight. J. E. Mackenzie and H. Marshall also add that on the persulphidic formula, the reaction between a thiosulphate and persulphate to form tetrathionate and sulphate is symbolized: $2(MSO_3)SH+(HSO_3)O.O(MSO_3)=(MSO_3)S.S(MSO_3)+2(MSO_3)OH$, and, if, as A. Gutmann supposed, the rupture of the peroxidic union in the persulphate is associated with the formation of an analogous union in the tetrathionate, the reaction is symbolized: $2(MS_2O_2)OM+(MSO_3)O.O(MSO_3)=(MS_2O_2)O.O(S_2O_2M)+2(MSO_3)OM$. Such a reaction would be of an exceptional character because peroxidic union cannot generally be brought about by iodine; rather is iodine liberated from iodides by peroxides or analogous compounds. J. E. Mackenzie and H. Marshall add that the striking point about A. Gutmann's reaction with an alkaline soln. of sodium arsenite is that instead of the arsenite removing sulphur only, oxygen is also removed to form arsenate and sulphoarsenate. To explain this without resorting to A. Gutmann's formula, it is merely necessary to assume that the first action of the alkaline arsenite soln. is not to remove oxygen or sulphur from the tetrathionate, but to add sodium and so reduce it to thiosulphate as in W. Spring's reaction; and the thiosulphate then reacts with the alkaline arsenite, forming sulphite and monosulpharsenate. If hydrochloric acid be added to a mixture of arsenate and iodide, arsenic trichloride and iodine are produced, but in the presence of alkali (carbonate), arsenite and iodine interact to form arsenate and iodide; similarly, when hydrochloric acid is added to a mixture of arsenate and thiosulphate, arsenic trichloride and tetrathionic acid are formed, and it may therefore be surmised that the change will be reversed in the presence of alkali, and that arsenite and alkali-lye will form arsenate and thiosulphate. A. Gutmann expected that an alkali cyanide would react with the tetrathionate, forming sulphite, cyanate, and thiocyanate, but the reaction is symbolized: $Na_2S_4O_6+2NaCy+2NaOH=Na_2SO_4+Na_2SO_3+2NaCyS+H_2O$. A. Gutmann said that the reaction is slow; but J. E. Mackenzie and H. Marshall found it is fairly rapid. The alkali is not necessary, but if omitted, twice as much cyanide is necessary to complete the change: $Na_2S_4O_6+4NaCy+H_2O=Na_2SO_3+Na_2SO_4+2NaCyS+2HCy$—the presence of a great excess of hydrocyanic acid seems to have no influence on the reaction. Instead of assuming that the tetrathionate is reduced to thiosulphate, it is assumed that the cyanide simply removes the two connecting sulphur atoms, leaving the two SO_3Na-groups, which then interact with formation of sodium sulphate and sulphur dioxide, thus: $2SO_2ONa=SO_2(ONa)_2+SO_2$, the sulphur dioxide would act either on the free alkali or, in its absence, on the cyanide, forming sodium sulphite. The formation of sulphate and sulphur dioxide from the two $NaSO_3$-groups would be to some extent analogous to one of the actions observed at the anode in certain electrolytic decompositions; for example, the formation of methyl acetate from two $CH_3.CO_2$-groups during the electrolysis of an acetate soln.: $2CH_3.CO_2=CH_3.CO_2.CH_3+CO_2$. The difference in the action of the alkaline arsenite soln. and of the alkaline cyanide soln. on tetrathionate is therefore easily explicable, using the persulphidic formula, and is due to the preliminary formation of thiosulphate in the first case and not in the other. E. Weitz found that the ammonium salts of monobasic acids are more soluble in ammonia than in water, while the salts of the polybasic acids are less soluble; by this test, dithionic acid is monobasic, or rather "doubly monobasic" $(HSO_3)_2$, since there are two separate nuclei in the molecule, each containing an acid-hydrogen atom.

F. Raschig assumed that in the reaction between hydrogen sulphide and sulphur dioxide a very labile SO-group is formed: $SO_2+H_2S=SO+S+H_2O$, and just as 3 mols. of acetylene condense at high temp. to form the benzene ring, so do five SO-groups condense to form the ring:



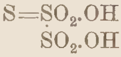
$$SO<\begin{matrix}SO.SO\\SO.SO\end{matrix}$$

which reacts with water to form pentathionic acid. He proposed the following formulæ for the polythionic acids:



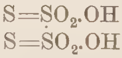
$$\begin{matrix}SO_2OH\\SO_2OH\end{matrix}$$

Dithionic acid.



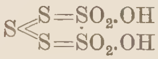
$$\begin{matrix}S=SO_2.OH\\SO_2.OH\end{matrix}$$

Trithionic acid.



$$\begin{matrix}S=SO_2.OH\\S=SO_2.OH\end{matrix}$$

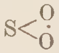
Tetrathionic acid.



$$S<\begin{matrix}S=SO_2.OH\\S=SO_2.OH\end{matrix}$$

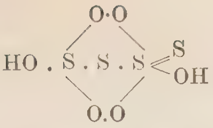
Pentathionic acid.

The SO_2-group is supposed to be constituted:

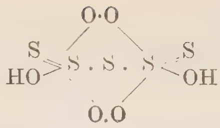


$$S<\begin{matrix}O\\O\end{matrix}$$

H. Debus, E. H. Riesenfeld and G. W. Feld, and F. Raschig pointed out that dithionic acid differs in many respects from the other thionic acids so that some exclude dithionic acid from the polythionic acid group. Thus, dithionic acid is produced by the oxidation of sulphur dioxide by pyrolusite, or potassium permanganate, whilst the other thionic acids are produced by the reduction of sulphur dioxide by hydrogen sulphide; also dithionic acid is comparatively stable and very slowly decomposed by boiling with conc. hydrochloric acid, whilst the remaining thionic acids are unstable and are readily decomposed under the same circumstances. Hence, it seems that the constitution of dithionic acid must differ from that of tri-, tetra-, and penta-thionic acids. J. A. Christiansen favoured the assumption that tetrathionic and pentathionic acids contain a six-membered ring, and said that the hypothesis is favoured by the bimolecular character of the vapour of sulphur trioxide. This corresponds with the formulæ:



Tetrathionic acid.



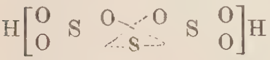
Pentathionic acid.

E. H. Riesenfeld and G. W. Feld suggest applying co-ordination formulæ to these acids, but they were not sure if the co-ordination number of sulphur is 4 or 6. F. Martin and L. Metz showed that the co-ordination number is 4, and valency +6; whilst the co-ordinated atoms have a valency of −2. Thus,

$$\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\left[\begin{matrix}\mathrm{O} & & \mathrm{O}\\ & \mathrm{S} & \\ \mathrm{O} & & \mathrm{O}\end{matrix}\right] \qquad \begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\left[\begin{matrix}\mathrm{O} & & \mathrm{O}\\ & \mathrm{S} & \\ \mathrm{S} & & \mathrm{O}\end{matrix}\right] \qquad \mathrm{H}\left[\begin{matrix}\mathrm{O} & & \mathrm{O}\\ & \mathrm{S} & \\ \mathrm{O} & & \mathrm{O}\end{matrix}\right].\left[\begin{matrix}\mathrm{O} & & \mathrm{O}\\ & \mathrm{S} & \\ \mathrm{O} & & \mathrm{O}\end{matrix}\right]\mathrm{H}$$

Sulphuric acid. Thiosulphuric acid. Perdisulphuric acid.

In the polythionic acids:



Trithionic acid.

$$\mathrm{H}\left[\begin{matrix}\mathrm{O} & & \mathrm{O}\\ & \mathrm{S} & \\ \mathrm{O} & & \mathrm{S}\end{matrix}\right].\left[\begin{matrix}\mathrm{O} & & \mathrm{O}\\ & \mathrm{S} & \\ \mathrm{S} & & \mathrm{O}\end{matrix}\right]\mathrm{H} \qquad \mathrm{H}\left[\begin{matrix}\mathrm{O} & & \mathrm{O}\\ & \mathrm{S} & \\ \mathrm{O} & & \mathrm{S}\end{matrix}\right]\mathrm{S}\left[\begin{matrix}\mathrm{O} & & \mathrm{O}\\ & \mathrm{S} & \\ \mathrm{S} & & \mathrm{O}\end{matrix}\right]\mathrm{H}$$

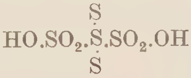
Tetrathionic acid. Pentathionic acid.

These formulæ explain the ready loss of a sulphur atom from the pentathionates; the interconversion of the polythionic acids; the presence of bivalent sulphur; their strong acidity; the non-formation of complex ions; and also H. Hertlein's measurements. I. Vogel added that these are the only formulæ for the polythionic acids which explain all the facts known at the present time. I. Vogel also suggested the formulæ

$$\begin{matrix}\mathrm{SO_2.OH}\\ \dot{\mathrm{S}}\mathrm{O_2.OH}\end{matrix} \qquad \mathrm{S}{<}\begin{matrix}\mathrm{SO_2.OH}\\ \mathrm{SO_3.OH}\end{matrix} \qquad \mathrm{S:S}{<}\begin{matrix}\mathrm{SO_2.OH}\\ \mathrm{SO_2.OH}\end{matrix} \qquad \mathrm{S:S:S}{<}\begin{matrix}\mathrm{SO_2.OH}\\ \mathrm{SO_2.OH}\end{matrix}$$

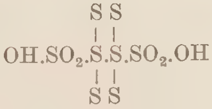
Dithionic acid. Trithionic acid. Tetrathionic acid. Pentathionic acid.

H. Bassett and R. G. Durrant agreed with this formula for trithionic acid, and also for tetrathionic acid, but there is probably a tautomeric form of tetrathionic acid (*q.v.*) with D. I. Mendeléeff's chain formula, stable in alkaline soln.; but they preferred the formula:



$$\mathrm{HO.SO_2.}\overset{\mathrm{S}}{\underset{\mathrm{S}}{\mathrm{S}}}\mathrm{.SO_2.OH}$$

for pentathionic acid; and added that it is the tendency of the central sulphur atom in trithionic acid, to become co-ordinated with four other atoms in all which is the prime cause of the readiness with which tetrathionic acid and pentathionic acids are built up from trithionic. This building-up process comes more or less to an end with the symmetrical pentathionate, and on these grounds the existence of hexathionic acid is improbable. Higher polythionates than pentathionate only seem likely if the two central sulphur atoms in the straight-chain form of tetrathionic acid can add on additional sulphur atoms in the same way as does the one central sulphur atom of trithionic acid. The building-up process in this case would come to an end with octothionic acid:



$$\mathrm{OH.SO_2.}\overset{\mathrm{S}}{\underset{\mathrm{S}}{\mathrm{S}}}.\overset{\mathrm{S}}{\underset{\mathrm{S}}{\mathrm{S}}}\mathrm{.SO_2.OH}$$

with hexa- and hepta-thionic acids as intermediate stages.

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§ 40. Dithionic Acid

In 1819, in their memoir : *Sur un acide nouveau formé par le soufre et l'oxygène*, J. L. Gay Lussac and J. J. Welter [1] described the preparation of what they called *l'acide hyposulfurique*. The composition was intermediate between that of sulphurous acid and that of sulphuric acid, and by analogy with hyposulphurous acid, it was called *hyposulphuric acid*, and later **dithionic acid,** $H_2S_2O_6$. J. L. Gay Lussac and J. J. Welter prepared the acid as follows : Dithionic acid is obtained by passing sulphur dioxide into water with manganese dioxide in suspension. The reaction takes place quickly, and a neutral soln. of manganese sulphate and dithionate is formed. An excess of baryta is added when the barium dithionate remains in soln. while the barium sulphate is precipitated. Carbon dioxide is passed through the filtrate which is then warmed to drive off the excess of carbon dioxide and precipitate any barium carbonate in soln. The liquid is evaporated for crystallization. The resulting barium dithionate is purified from calcium salts by recrystallization, and decomposed by sulphuric acid so as to precipitate the barium as sulphate, and liberate the dithionic acid. The aq. soln. of the acid is without odour ; and when exposed over conc. sulphuric acid in vacuo, at 10°, the liquid can be concentrated until its sp. gr. is 1·347 without volatilization. If the concentration be carried much further the liquid decomposes into sulphur dioxide and sulphuric acid. J. J. Berzelius recommended removing any manganese hydroxide from the manganese dioxide by means of nitric acid, otherwise sulphate is also formed later on ; and W. Delffs added that if the manganese dioxide contains iron, none of that element passes into soln. F. Heeren employed five parts of water to one part of finely powdered manganese dioxide; treated the filtrate with barium sulphide, instead of the hydroxide, and after treatment with carbon dioxide, boiled the liquid to drive off the carbon dioxide and hydrogen sulphide, and precipitate the barium carbonate. The filtered liquid was evaporated for crystallization. F. Heeren said that the equation $MnO_2+2SO_2=MnS_2O_6$ does not represent the reaction because the dithionate is always accompanied by manganese sulphate in amounts varying from about 12 to 26 per cent. The amount of sulphate formed is greater, the higher the temp., and the coarser the powder of manganese dioxide. W. Spring and L. Bourgeois said that nine times as much sulphate may be produced as dithionate, and the amount is greater the higher the temp. and the finer the powder. F. Heeren added that if the dioxide also contains the lower oxide sulphate and sulphite will be produced: $Mn_2O_3+2SO_2=MnSO_4+MnSO_3$. On the other hand, W. Spring and L. Bourgeois represented the formation of sulphate in the production of manganese dithionate, $MnO_2+2H_2SO_3=2H_2O+MnS_2O_6$, as a side-reaction $MnO_2+SO_2=MnSO_4$; J. Meyer considered that, in the cold, manganic sulphite is formed as an intermediate product: $2MnO_2+3H_2SO_3=Mn_2(SO_3)_3+3H_2O+O$; followed by $Mn_2(SO_3)_3=MnSO_3+MnS_2O_6$, and $MnSO_3+O=MnSO_4$; and added that manganous but not manganic sulphite can be detected in the liquid. F. Heeren found that liquid sulphur dioxide has no action on manganese dioxide. F. von Hauer prepared the alkali dithionates by boiling aq. soln. of alkali sulphites with manganese dioxide; and H. Baubigny, by boiling a soln. of potassium silver sulphite; he also made sodium dithionate as follows:

Boil for half an hour an aq. soln. of silver nitrate (9 grms.) with sodium sulphite (20 grms.). The clear liquid is treated with barium nitrate, followed by slight excess of sodium carbonate; after filtration, it is neutralized exactly with nitric acid and evaporated to crystallization. The product is purified from sodium nitrate by taking advantage of the greater solubility of the latter in 50 per cent. alcohol.

J. L. Gay Lussac and J. J. Welter said that lead or barium dioxide does not act in the same way. This was confirmed by H. C. H. Carpenter, while C. F. Rammelsberg added that lead dioxide has scarcely any action on sulphurous acid; barium, magnesium, and sodium dioxides produce sulphates; and mercuric oxide gives no dithionate. R. Hac obtained dithionates by oxidizing warm, aq. soln. of the normal alkali sulphites with red-lead—manganese dioxide was ineffective. The milder oxidizing agents represented by the hydroxides of the tervalent iron family give better results, and A. Gélis prepared the dithionate by passing sulphur dioxide into water with ferric hydroxide in suspension. The red soln. which is formed was first observed by P. Berthier, and, as proved by K. Seubert and M. Elten, it consists of a soln. of ferric sulphite: $2Fe(OH)_3+3SO_2=Fe_2(SO_3)_3+3H_2O$. H. C. H. Carpenter observed that while freshly precipitated, unwashed ferric hydroxide is quickly dissolved by sulphurous acid, the hydroxide quickly ages, even during the washing, and the speed of the reaction rapidly slows down. A. Gélis found that when the liquid is allowed to stand for some time, it becomes dark green owing to the formation of ferrous sulphite and dithionate: $Fe_2(SO_3)_2=FeSO_3+FeS_2O_6$. In support of this hypothesis, M. J. Fordos and A. Gélis observed that ferric sulphite decomposes in this manner. A. Gélis added baryta-water to the liquid, and treated the filtered soln. of barium dithionate as in J. L. Gay Lussac and J. J. Welter's process. U. Antony said that the reaction proceeds further, for some of the ferrous sulphite is oxidized by the sulphuric acid to form dithionate: $FeSO_3+H_2SO_4=H_2O+FeS_2O_6$. J. Meyer denied that this reaction really occurs. He said that sulphuric acid is stronger than sulphurous acid, and that it makes no difference whether sulphurous acid is added to a sulphate or sulphuric acid added to a sulphite, in no case is any dithionate formed with soln. of ferrous or manganous salts and sodium sulphite or hydrosulphite. U. Antony and E. Manasse said that both manganous and ferrous sulphites react with sulphuric acid to form dithionate. J. Meyer stated that ferric, cobaltic, and nickelic hydroxides oxidize sulphurous acid to dithionic acid and the sulphite of the bivalent metal. H. C. H. Carpenter believed that the ferric salt employed by A. Gélis contained some manganese as impurity. H. C. H. Carpenter's results with these hydroxides are shown in Table XVIII, along with the heats of the reduction typified by $2Fe(OH)_3=2Fe(OH)_2+O+H_2O-546$ cals. It therefore follows that the greater the energy required for the reduction of the hydroxides, the larger the percentage yield of dithionic acid. The energy needed for the reaction with ferric hydroxide is such that the process stops at the stage: $2Fe(OH)_3+3SO_2=FeS_2O_6+FeSO_3+3H_2O$; very little, if any, is expended in the reaction $FeS_2O_6=FeSO_3+SO_3$, although with manganic hydroxide about a quarter, and with cobaltic hydroxide about two-thirds, of the dithionate formed is decomposed in this manner. In the exothermic process with nickelic hydroxide, the energy suffices to convert all the dithionate to sulphite. P. Berthier found that potassium chromate or dichromate oxidizes sulphurous acid to dithionate and sulphate, and H. Bassett observed that when chromic acid, or potassium chromate or dichromate, is reduced by sulphurous acid, 94 to 95 per cent. of sulphate and 5 to 6 per cent. of dithionate are formed, and that the results are independent of the temp.

TABLE XVIII.—THE OXIDATION OF SULPHUROUS TO DITHIONIC ACID BY THE HIGHER HYDROXIDES OF THE IRON FAMILY.

Hydroxides.	Dithionate per cent.	Sulphate per cent.	Heat of reduction in cals.
$Fe(OH)_3$ . . .	96·19	—	−546
$Mn(OH)_3$ . . .	75·02	25·42	−448
$Co(OH)_3$ . . .	36·02	63·56	−225
$Ni(OH)_3$ . . .	Nil	101·04	+13

U. Antony and A. Lucchesi found that ruthenium sulphate acts as an oxidizing agent on sulphurous acid, forming the dithionate: $Ru(SO_4)_2+SO_2+2H_2O=RuSO_4+2H_2SO_4$; and $RuSO_4+SO_2=RuS_2O_6$; A. Benrath and K. Ruland, ceric sulphate; and U. Antony and E. Manasse found that ferric sulphate reacts similarly $Fe_2(SO_4)_3+3SO_2+2H_2O=2FeS_2O_6+2H_2SO_4$—there is an 80 per cent. yield of dithionate at 0°, whilst none is formed at 95°. Sulphates of the type $FeSO_4$ do not react like $RuSO_4$, for they produce no dithionate with sulphurous acid. J. Meyer said that in the case of ruthenic sulphate, $Ru(SO_4)_2$, the sesquisulphate, $Ru_2(SO_4)_3$, is first formed; this reacts with sulphurous acid, forming the sesquisulphite, which then decomposes into ruthenous sulphite and dithionate as in the case of ferric sulphite. J. Meyer said that dithionates are not produced by the action of normal or acid sulphites or of sulphurous acid on ferrous sulphate or manganous sulphate, this being eq. to the action of sulphuric acid or a sulphate on the corresponding sulphite. There are other ways of oxidizing sulphurous acid, or sulphites to dithionates. Thus, V. A. Jacquelain, and F. Rochleder stated that when soln. of sulphurous acid, or ammonium hydrosulphite, are exposed with imperfect access to air for a few years, sulphate and dithionate are produced. M. Berthelot found that a soln. of persulphuric acid in sulphuric acid will oxidize sulphurous acid to dithionic acid; and B. Rathke and co-workers obtained a similar result with selenium and alkali sulphite —it is assumed that a selenotrithionate is first formed which then decomposes into alkali dithionate and selenium: $K_2S_2SeO_6=K_2S_2O_6+Se$. F. Heeren, and T. S. Dymond and F. Hughes observed that acidic soln. of potassium permanganate oxidize sulphurous acid to dithionates. H. Buignet said that the permanganate is first reduced to manganese dioxide which then acts as indicated above: $2KMnO_4+6SO_2+2H_2O=2KHSO_4+2MnSO_4+H_2S_2O_6$—each mol. of dithionate is accompanied by 4 mols of sulphate. L. P. de St. Gilles, and M. J. Fordos and A. Gélis said that in alkaline soln., the sulphite is almost completely oxidized to sulphate. N. Sokoloff and P. L. Maltschewsky said that a dil. soln. of iodine in potassium iodide will oxidize alkali hydrosulphite to dithionates, $2NaHSO_3+2I=2NaI+H_2SO_6$

—the yield is about 20 per cent. of the theoretical, the rest passes into sulphate; W. Spring and co-workers said that no dithionate is formed since the reaction progresses: $2NaHSO_3+4I+2H_2O=4HI+2NaHSO_4$. R. Otto at first confirmed and later denied that dithionate is formed. A. Friessner and co-workers studied the electro-oxidation of neutral or alkaline (not acidic) soln. of sodium sulphite with a high anodic potential. By polarizing a platinized platinum anode anodically in a soln. of sodium hydroxide before use, the formation of dithionate is insured, whereas a cathodically polarized or a depolarized electrode gives no dithionate. A smooth platinum anode soon becomes polarized in the sulphite soln. itself sufficiently to produce dithionate even if it is initially depolarized. The formation of dithionate is favoured by a rise of temp. to 60°–70°; it is practically unaffected by the conc. of the sulphite soln. The latter fact together with the fact that it is not formed in acidic soln. shows that the dithionate is produced from SO_3'' ions, and the reaction is represented: $2SO_3''+2OH'+2H^{\cdot}+2\oplus=S_2O_6''+2H_2O$. A soln. of dithionic acid or of one of its salts is not reduced at the cathode, and undergoes very little oxidation at the anode. According to O. Essin, the addition of up to 0·1 per cent. of ammonium fluoride to the electrolyte increases the yield of dithionate, but a higher proportion lessens the yield; a pre-ignition of the anode, and a pre-polarization of the anode increase the yield of dithionate. Under favourable conditions no more than a 45 per cent. yield of dithionate could be obtained.

A. Nabl observed that when a 33 per cent. soln. of sodium thiosulphate is mixed with the calculated quantity of hydrogen dioxide, and an acid added from time to time to keep the liquid neutral, sodium dithionate is formed: $2NaS_2O_3+H_2O_2=2NaOH+Na_2S_2O_6$; if an excess of hydrogen dioxide is used, the dithionate is oxidized to sulphate: $H_2S_2O_6+H_2O_2=2H_2SO_4$; and in an alkaline soln., $16Na_2S_2O_3+8H_2O_2=12Na_2S_2O_3+2Na_2SO_4+Na_2S_2O_6+Na_2S_4O_6+8H_2O$. L. P. de St. Gilles observed that an acidic soln. of potassium permanganate oxidizes thiosulphate to dithionate; and M. Hönig and E. Zatzek, and C. Luckow observed the reaction occurs in acetic acid soln.; in boiling neutral soln., J. Stingl and T. Morawsky said that some dithionate is probably formed along with the sulphate—*vide supra*, thiosulphuric acid.

M. J. Fordos and A. Gélis observed that trithionates furnish dithionates when treated with an acidic soln. of potassium permanganate. J. Meyer observed that acidic and alkaline soln. of hyposulphurous acid are oxidized by hydrogen dioxide to sulphuric and dithionic acids; and H. A. Bernthsen, by iodine in a similar way. H. Beckurts and R. Otto observed that dithionic acid is probably formed at an intermediate stage in the slow thermal decomposition of chlorosulphonic acid into sulphur dioxide, sulphuric acid, etc. H. Bunte observed the formation of sodium dithionate when sodium ethyl thiosulphate is heated to 100°. F. Raschig obtained dithionates by the action of an acidified soln. of potassium permanganate on trithionates.

Neither dithionic acid, nor **dithionic anhydride,** S_2O_5, has been isolated. The acid is known only in aq. soln. J. L. Gay Lussac and J. J. Welter found that when the aq. soln. of the acid is evaporated in vacuo over conc. sulphuric acid, at ordinary temp., it decomposes when the sp. gr. exceeds 1·347, and the aq. soln. also decomposes when warmed, forming sulphuric acid and sulphur dioxide, $H_2S_2O_6=H_2SO_4+SO_2$. The aq. soln. of dithionic acid is as clear as water; it is without smell; and has an acidic taste. J. S. Stas noted a slight decomposition when the aq. soln. has been kept a little while; and W. C. de Baat found that a 3–4 per cent. aq. soln. of dithionic acid is decomposed into sulphuric and sulphurous acids to the extent of 3 per cent. in 945 hrs. at 25°; and 20 per cent. in 245 hrs. at 47°. The alkali and alkaline earth salts are stable both in the solid state, and in aq. soln., but the salts of the heavy metals are not so stable. K. Klüss said that the aq. soln. of the alkali and alkaline earth dithionates can be heated to 100° without decomposition, though the solid salts decompose into sulphur dioxide and sulphate when heated to 100°. Dil. aq. soln. of the heavy metals decompose when boiled, and conc. soln. may give off sulphur dioxide at 50°.

Dithionic acid was analyzed by J. J. Berzelius; and the salts by F. Heeren, K. Klüss, K. Kraut, R. Otto, etc. J. J. Berzelius, and H. Kolbe thought that the acid is monobasic; and forms acid salts as well as complex salts. H. Frey also showed that the acid behaves like many monobasic acids in having its solvent action increased by the addition of neutral salts—W. Ostwald having showed that with polybasic acids, the solvent action is decreased by this treatment. H. Frey, therefore, gave HSO_3 for the formula and regarded it as analogous in many respects to hydrochloric acid. The analogy was weakened when he found that methylene disulphonic acid also behaves like hydrochloric acid. K. Klüss, and E. Weitz also doubted the dibasicity of the acid. W. Ostwald, however, found that the increase in the electrical conductivity of the sodium salt with dilution—**1.** 15, 13—indicates that the acid is dibasic; and this was confirmed by J. Meyer's observations on the conductivity of the barium salt, and on the lowering of the f.p. of water by the sodium and barium salts. H. Hertlein's observations on the conductivity of the acid support the view that the acid is dibasic—*vide supra*, the constitution of the polythionic acids. E. Weitz and H. Stamm studied the subject. A. C. Schultz-Sellack pointed out that the dithionate is not formed by the union of potassium sulphite and sulphur trioxide, so that the acid is only formally intermediate between pyrosulphuric acid, $H_2S_2O_7$, and pyrosulphurous acid, $H_2S_2O_5$.

E. Cornec found that the curves corresponding with the lowering of the f.p. or with the index of refraction of a soln. of dithionic acid during its progressive neutralization with a soln. of sodium hydroxide have each one break corresponding with the normal salt. M. Berthelot calculated for the heat of formation $(2S,5O,H_2O,Aq.)=206{\cdot}8$ Cals.; J. Thomsen, $(2SO_2,O,Aq.)=68{\cdot}95$ Cals.; $(2SO_2aq.,O)=53{\cdot}55$ Cals.; $(SO_3aq.,SO_2aq.)=-10{\cdot}08$ Cals.; $(2S,6O,2HAq.)=279{\cdot}45$ Cals.; $(2S,5O,Aq.)=211{\cdot}09$ Cals.; for the heat of neutralization, $2NaOHaq.+S_2O_5aq.=Na_2S_2O_6+H_2O+Aq.=27{\cdot}07$ Cals.; and for the heat of oxidation to sulphuric acid, 73·74 Cals. W. J. Pope gave 34·39 for the refraction eq. of the S_2O_6-radicle. R. Winger calculated values for the valency of the sulphur atoms in the dithionates from the X-ray spectrum. W. Ostwald found the electrical conductivity of soln. of a gram-equivalent of the acid in v litres of water at 25°, to be:

v . .	4	16	64	256	1024	4096
λ . .	79·4	83·2	87·3	90·0	91·6	90·7

and H. Hertlein, working at the same temp., found the conductivity, λ, and the degree of ionization, α, to be:

v . .	43·18	86·36	172·72	345·44	690·88	1381·76
λ . .	368·8	378·3	384·8	391·7	395·5	397·4
α . .	0·896	0·920	0·935	0·952	0·961	0·966

where the conductivity is expressed in mercury units. The high degree of ionization of the acid indicates that it must be regarded as a strong acid. The transport number calculated from observations with the sodium salt is 86·4; with the potassium salt, 83·5; with the barium salt, 75·5; and with the thallium salt, 96·5, K. Jellinek attempted to calculate values for the ionization constant of the acid, but found that the mass law did not apply; M. Rudolphi calculated values for the degree of ionization and the ionization constant on the assumption that dithionic acid is monobasic.

According to D. M. Yost and R. Pomeroy, the rate of decomposition of dithionic acid into sulphurous and sulphuric acids, at 50° and at 80°, and in the presence of different proportions of hydrochloric or perchloric acid, is proportional to the conc. of the dithionate and to that of the total acid, provided its conc. does not exceed $0{\cdot}6N$; but at higher acid conc., the rate increases more rapidly. These facts indicate that the catalytic effect of the acid is probably one of hydrolysis. W. Spring and L. Bourgeois found that dithionic acid is reduced by nascent **hydrogen** from sodium amalgam, to sulphurous acid. R. Otto obtained a similar result with zinc and hydrochloric acid—even at 0°; and he added that the dithionic acid is not split into sulphur dioxide and sulphuric acid. Oxidizing agents can transform dithionic acid into sulphuric acid, but as stated by A. Fischer and W. Classen, sodium dithionate is not readily attacked by cold alkaline or neutral oxidizing agents, and but little in acid soln. All the dithionates tried were reported by J. L. Lussac and J. J. Welter, and F. Heeren to be soluble in **water.** A. Longi and L. Bonavia found that **sodium dioxide** very slowly oxidizes the dithionates to sulphates. F. Heeren said that the acid is not oxidized by **lead dioxide ;** R. F. Weinland and J. Alfa found that when the alkali dithionates are treated with **hydrofluoric acid,** the hydroxyl-group of the acid is replaced by fluorine, and fluodithionates are formed. J. L. Gay Lussac and J. J. Welter, and F. Heeren found that dithionic acid is not affected by cold hydrochloric acid, but when the liquid is boiled, the dithionate or dithionic acid is resolved into sulphurous acid and a sulphate without the deposition of sulphur. Hence, when an acidic soln. of the dithionate has been boiled a few minutes, it decolorizes potassium permanganate, precipitates sulphur from a soln. of hydrogen sulphide, and separates gold from a soln. of gold chloride. J. L. Gay Lussac and J. J. Welter said that the cold aq. soln. of the acid is not oxidized by an aq. soln. of **chlorine,** but it is oxidized in a boiling soln.; and A. J. Balard found that the cold soln. is not oxidized by **hypochlorous acid.** J. A. Muller found that the action of **iodine** on dithionates is so slow in cold neutral soln. or in soln. acidified with acetic acid as not to interfere with the titration of thiosulphates by iodine soln. The action is faster with warm soln., and it proceeds according to the equation $Na_2S_2O_6+I_2+2H_2O=2NaHSO_4+2HI$. J. A. Muller found that the reaction is unimolecular, and it is therefore assumed that it occurs in 3 stages: (i) the liberation of dithionic acid (fast); (ii) the decomposition of the dithionic acid into sulphurous and sulphuric acids (slow); and (iii) the action of iodine on sulphurous acid (fast). Only the velocity of the second reaction is therefore measured. The velocity constant is 0·00836 at 51·3°. C. Mayr and I. Szentpaly-Peyfuss observed that while dithionic acid is not affected by bromine in the cold, it is completely oxidized to sulphuric acid by bromates in boiling hydrochloric acid soln. According to D. M. Yost and R. Pomeroy, the rate of oxidation of dithionic acid by dichromate, bromate, and iodate is about the same for these three oxidizing agents, and is independent of their conc., and nearly identical with the rate of the decomposition of the acid into sulphurous and sulphuric acids. This shows, as J. A. Muller concluded in the case of its oxidation by iodine, that the first step in the oxidation of dithionic acid is commonly, if not always, its hydrolysis, and that the sulphurous acid thereby produced is then oxidized. F. Heeren found that dithionic acid does not decompose **hydriodic acid ;** nor does it attack **hydrogen sulphide.** H. C. H. Carpenter found that while barium dithionate is not changed by **sulphur dioxide,** lead dithionate yields lead sulphite and dithionic acid. J. L. Gay Lussac and J. J. Welter, and F. Heeren observed that solid dithionates are decomposed by **sulphuric acid** at ordinary temp. with the escape of sulphur dioxide; but in aq. soln., the effects resemble those produced by hydrochloric acid. J. L. Gay Lussac and J. J. Welter said that a cold soln. of dithionic acid is not oxidized by conc. **nitric acid.** H. Baubigny said that dithionic acid cannot be completely oxidized to sulphuric acid by heating it with aqua regia in open or closed vessels. He oxidized a soln. of dithionate to sulphate by an excess of sodium carbonate and nitrate. K. Kraut observed that when a dry dithionate is heated with **phosphorus pentachloride,** thionyl and phosphoryl chlorides are produced; and it is also decomposed by **phosphoryl chloride.** A. Gutmann found that sodium dithionate is not reduced by **sodium arsenite** at ordinary temp. According to J. L. Gay Lussac and J. J. Welter, dil. dithionic acid dissolves zinc with the evolution of hydrogen, without decomposing the acid; and F. Heeren obtained a similar result with **iron.** P. Neogi and R. C. Bhattacharyya found that dithionates are not reduced by **magnesium amalgam.** J. L. Gay Lussac and J. J. Welter, F. Heeren, and A. Longi and L. Bonavia observed that in the cold, dithionates and dithionic acid are not oxidized by **potassium permanganate.** F. Heeren said that the acid is not oxidized by

salts of silver, gold, mercury, and platinum—*vide* Table XVIII. Dithionates are not decomposed by boiling with alkali-lye. A. Gutmann said that sodium dithionate is not reduced by **sodium stannite** at ordinary temp.

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§ 41. The Dithionates

Only normal and basic dithionates of the dibasic dithionic acid are known; acid salts have not been obtained. F. Heeren[1] obtained ill-defined, hair-like crystals of **ammonium dithionate,** $(NH_4)_2S_2O_6.\frac{1}{2}H_2O$, by evaporating, at ordinary temp., the filtrate from the double decomposition of ammonium sulphate, and barium dithionate. K. Klüss obtained aggregates of colourless needles, which A. Fock said are monoclinic, with the cleavage on the (010)-face perfect. K. Klüss said that when heated for 3 hrs. at 75°, or allowed to stand over conc. sulphuric acid, it loses 4·42–4·84 per cent. of water; and at 130°, the salt is decomposed; and F. Heeren said that when the salt is heated, it loses 18·44 per cent. of water, sulphur dioxide is also given off, and ammonium sulphate remains. W. C. de Baat found that the salt lost 4·51 per cent. in weight at 70°; another 0·14 per cent. at 130°; 3·97 per cent. at 150°; 30·49 per cent. at 160°; and 32·78 at 165°. The solubility of the hemihydrate is 57·05 per cent. at 0°; 60·14 at 10°; 62·43 at 20°; and 64·60 at 30°. F. Heeren said that 100 parts of water at 16° dissolve 114·9 parts of the hemihydrate —K. Klüss said 178·6 parts are dissolved at 19°; both observers found that the aq. soln. can be boiled without decomposition; and that the salt is insoluble in absolute alcohol. H. Stamm measured its solubility in aq. ammonia and found that soln. with 0, and 6·882 mols of NH_3 per 100 grms. of water, dissolved respectively 1·508 and 2·066 mols of $(NH_4)_2S_2O_6$. K. Klüss observed that an isomorphous series of complex salts is formed with the dithionates of bivalent zinc, cadmium, manganese, iron, cobalt, and nickel. A. Fock and K. Klüss observed that the evaporation of a mixed soln. of ammonium dithionate and chloride furnishes rhombic, bipyramidal crystals of **ammonium chlorodithionate,** $(NH_4)_2S_2O_6.NH_4Cl$, with the axial ratios $a:b:c=0·9827:1:0·9612$; perfect cleavage on the (100)-face; and with the optic axial angle $2E=40°$ nearly.

A. P. Sabanéeff evaporated, at a low temp., the filtrate from a mixed soln. of barium dithionate and hydroxylamine sulphate, and obtained crystals of **hydroxylamine dithionate,** $(NH_2OH)_2.H_2S_2O_6$, resembling those of ammonium nitrate. If the soln. be evaporated on the water-bath, it is partially decomposed, and at 120°, sulphur dioxide escapes, hydroxylamine sulphate remains. The salt is a strong reducing agent. The analysis agrees with the above formula, which is isomeric with ammonium persulphate. Cryoscopic observations on the aq. soln. indicated that a mol. of the salt furnishes three ions. A. P. Sabanéeff also obtained long, prismatic crystals of **hydrazine hydrodithionate,** $N_2H_4.H_2S_2O_6$, *i.e.* $N_2H_5.HS_2O_6$, in an analogous manner. The salt is easily soluble in water, and the soln. decomposes after standing some time. When the aq. soln. is evaporated over conc. sulphuric acid, it yields a mixture of hydrazine sulphate, and **hydrazine dithionate,** $2N_2H_4.H_2S_2O_6$, *i.e.* $(N_2H_5)_2S_2O_6$, which is easily obtained by adding barium dithionate to a soln. of hydrazine sulphate previously neutralized with hydrazine hydrate.

C. F. Rammelsberg prepared **lithium dithionate,** $Li_2S_2O_6.2H_2O$, by double decomposition with barium dithionate and lithium sulphate. H. Topsöe gave 2·158 for the sp. gr. of the rhombic, bipyramidal crystals which, according to H. Topsöe and C. Christiansen, have the axial ratios $a:b:c=0·9657:1:0·5779$. The (100)-cleavage is perfect, the optic axial angle $2V=78° 16'$, and $2E=159° 45'$; and the indices of refraction respectively for the C-, D-, and E-lines are $\alpha=1·5462$, 1·5487, and 1·5548; $\beta=1·5565$, 1·5602, and 1·5680; and $\gamma=1·5765$, 1·5788, and 1·5887. A. F. Hallimond discussed the mol. vol. C. F. Rammelsberg found that the crystals become moist when exposed to air; they are easily soluble in water; and when heated on the water-bath they lose their water of crystallization; and at a higher temp., sulphur dioxide is given off, and lithium sulphate remains.

H. Bunte obtained anhydrous **sodium dithionate,** $Na_2S_2O_6$, by heating sodium ethyl thiosulphate to 100°, when: $2(NaO.SO_2.SC_2H_5)=Na_2S_2O_6+(C_2H_5)_2S_2$. F. Heeren obtained the *dihydrate*, $Na_2S_2O_6.2H_2O$, by crystallization from the aq. soln. obtained by adding sodium carbonate to a boiling soln. of barium or calcium dithionate and filtering. N. Sokoloff and P. L. Malschewsky obtained it by the action of iodine on sodium hydrosulphate; W. Spring and L. Bourgeois did not succeed in the preparation, but R. Otto and A. Holst obtained the salt by treating a dil. soln. of sodium hydrosulphate with a dil. soln. of iodine in one of potassium iodide, neutralizing with sodium hydroxide, and evaporating the liquor. The dihydrate can also be precipitated from its aq. soln. by alcohol. K. Kraut said that the cooling of the aq. soln. of the salt, saturated with sulphur dioxide, furnishes crystals of the hexahydrate, $Na_2S_2O_6.6H_2O$, which resemble those of sodium phosphate. R. Hac obtained a 75 per cent. yield by heating one part each of sodium sulphite and lead dioxide with two parts of water until all the sulphite had dissolved; passing in carbon dioxide; filtering; neutralizing with lactic acid; and concentrating for crystallization. The clear, prismatic crystals of the dihydrate were examined by F. Heeren, C. F. Rammelsberg, J. Grailich and V. von Lang, and A. des Cloizeaux. The axial ratios of the rhombic bipyramidal crystals were found by H. Baker to be $a:b:c=0·9922:1:0·5981$; and the (110)-cleavage is perfect. C. Gaudefroy studied the dehydration figures. J. Grailich and V. von Lang gave $2V=73° 26'$ for red-light; 75° 14′ for yellow-light; and 76° 28′ for green-light; and $2E=126° 38'$ for red-light, and 126° 4′ for blue-light; while A. des Cloizeaux gave $2E=126° 4'$ for red-light; 129° 33′ for yellow-light; and 139° 2′ for blue-light. There is no perceptible change in these angles when the crystals are heated to 75°. J. Grailich and V. von Lang studied the corrosion figures. H. Topsöe gave 2·189 for the sp. gr.; P. Groth, 2·196; and H. Baker, 2·175 at 11°. A. F. Hallimond discussed the mol. vol. F. A. H. Schreinemakers and B. C. van B. Walter studied the osmosis of aq. soln. J. Thomsen gave for the heat of formation $(2Na,O_2,2SO_2)=256·65$ Cals.; $(2Na,O_2,2SO_2,2H_2O)=262·93$ Cals.; and $(Na_2SO_4,SO_2)=-0·86$ Cal. The heat of neutralization, $(NaOHaq.,S_2O_5aq.)=27·07$ Cals.; and the heat of soln. of the anhydrous salt in 400 mols of water at 18° is −5·37 Cals.; and of the dihydrate, −11·65 Cals. J. Grailich and V. von Lang found for red-, yellow-, and green-light, the respective indices of refraction $\alpha=1·4803$, 1·4820, and 1·4838; $\beta=1·4927$, 1·4953, and 1·4978; and $\gamma=1·5158$, 1·5185, and 1·5212. V. J. Sihvonen found maxima in the ultra-red reflection spectrum of sodium dithionate at 8·2μ, 10·1μ, 17·3μ, and 19·4μ. P. Bary observed that sodium dithionate is fluorescent when exposed to the X-rays. W. Ostwald gave for the electrical conductivity of a mol of the salt in v litres of water:

v	32	64	128	256	512	1064
μ	109·6	116·1	120·6	123·4	126·7	130·4

C. Watkins and H. C. Jones found the molar conductivity, μ mhos, and percentage ionization, α, of soln. with a mol of salt in v litres:

	v	8	16	32	128	512	1024	2048	4096
μ	0°	91·28	99·71	107·8	121·4	130·6	137·1	139·1	139·1
	15°	135·9	147·6	161·7	180·9	195·6	203·6	208·4	207·3
	25°	167·8	183·9	200·5	225·0	242·8	255·0	259·4	258·2
	35°	202·6	220·3	241·6	272·5	293·9	308·6	314·3	312·7
α	0°	65·6	71·6	77·5	87·2	93·8	98·6	100·0	100·0
	35°	64·4	70·1	76·8	86·7	93·5	98·1	100·0	100·0

C. Pape found that the crystals of the dihydrate begin to effloresce at 55°. W. C. de Baat found that the salt lost 18·85 per cent. at 130°; 14·89, at 150°; 15·13, at 170°; 15·51, at 182°; 18·34, at 195°; 36·50, at 235°; and 41·23, at a red-heat. The solubility of the dihydrate is 6·05 per cent. at 0°; 10·63, at 12°; 13·39, at 20°; and 17·32, at 30°. F. Heeren said that 100 parts of water at 16° dissolve 47·6 parts of salt, and 90·9 parts of salt at 100°. Boiling does not decompose the aq. soln. J. Cornog and W. E. Henderson said that a N-soln. of sodium dithionate is not decomposed by prolonged boiling, but, when heated in closed tubes at 150°, complete decomposition occurs within 6 hours. In the presence of excess of air the final reaction is $MS_2O_6+H_2O+O=MSO_4+H_2SO_4$, but in an inert atmosphere the reaction is more complex. Decomposition is favoured by increasing conc. and low press., and is accelerated by the initial presence of sulphur dioxide. The primary decomposition probably results in the formation of metallic sulphate and sulphur dioxide, and is followed by secondary reactions in which sulphur or sulphuric acid are formed. The salt does not dissolve in alcohol; and it is precipitated by fuming hydrochloric acid from its aq. soln. H. Stamm measured its solubility in aq. ammonia. W. Spring observed that the aq. soln. is reduced to sulphite by sodium amalgam.

F. Heeren made **potassium dithionate,** $K_2S_2O_6$, from the liquid obtained by heating an aq. soln. of barium dithionate with potassium sulphate or carbonate, or manganese dithionate with potassium hydroxide; F. von Hauer, from the liquid obtained by boiling potassium sulphite with manganese dioxide; and B. Rathke, from the soln. obtained by digesting potassium hydrosulphite with lead dioxide. F. Heeren said that the clear, colourless, prismatic crystals belong to the hexagonal system; and, according to C. S. Weiss, the crystals are trigonal with the axial ratio $a : c = 1 : 0·6467$, and $\alpha = 108° 27'$. Measurements were also made by A. Fock, E. Bichat, and V. von Lang. Twinning was observed by A. Fock, and he also observed the corrosion figures produced by sulphuric acid. M. L. Huggins and G. Frank found that the X-radiograms of the hexagonal crystals show that the space lattice has the dimensions $a = 9·8$ A., and $c = 6·45$ A., and contains 6K, 6S, and 18O atoms. The S-atoms are in pairs on the three-fold symmetry axis, each S-atom having three O-atoms symmetrically placed around it. H. Topsöe gave 2·277 for the sp. gr., and H. Hertlein, 2·277 to 2·280. H. Hertlein gave 104·64 for the mol. vol. The sp. gr. of soln. with 1·183, 3·003, and 5·618 per cent. of salt were found by H. Hertlein to be 1·00804, 1·02045, and 1·03860 respectively at 20°, and the mol. vol. respectively 77·728, 79·284, and 80·685. M. Berthelot gave 411·40 Cals. for the heat of formation of the salt from its elements; F. Martin and L. Metz, 415 Cals.; and J. Thomsen, 415·72 Cals. J. Thomsen gave for the heat of soln. in 400 mols of water at 18°, —13·01 Cals.; the heat of neutralization, $2KOHaq. + H_2S_2O_6aq. = K_2S_2O_6aq. + 27·07$ Cals. H. Topsöe and C. Christiansen found for the indices of refraction $\omega = 1·4532$, and $\epsilon = 1·51195$ for the C-line; $\omega = 1·4550$, and $\epsilon = 1·5153$ for the D-line; and $\omega = 1·4595$, and $\epsilon = 1·5239$ for the F-line. A. Ehringhaus and H. Rose studied the refractive index and dispersion. C. Pape found that crystals of the salt are optically active; the same salt may deposit dextro- and lævo-rotatory crystals; the sp. rotatory power is about one-third the value of quartz, being 6° 18′ for the C-line; 8° 39′ for the D-line; 10° 51′ for the E-line; and 12° 33′ for the F-line. E. Bichat gave 8° 7′ for the D-line. The aq. soln. are inactive. H. Hertlein gave for the sp. refraction of an aq. soln. of the salt at 20° for Na-light respectively with the μ- and the μ^2-formulæ to be 0·2108 and 0·1246, and for the mol. refractions respectively 50·25 and 28·71. V. J. Sihvonen found reflection maxima in the ultra-red spectrum of solid sodium dithionate at $8·2\mu$, $10·2\mu$, $17·6\mu$, and $19·3\mu$. P. Bary found that potassium dithionate is not fluorescent when exposed to the X-rays. H. Hertlein gave for the electrical conductivity, μ, of soln. of a mol of the salt in v litres of water at 25°:

v . .	32	64	128	256	512	1024	∞
μ . .	121·4	128·9	135·3	140·2	144·8	148·0	154·1

W. G. Hankel and E. Lindenberg studied the piezoelectricity of the crystals, which resembles that of quartz. F. Heeren found that the salt has a bitter taste, is stable in air, decrepitates when heated, and then decomposes, leaving a residue of potassium sulphate. W. C. de Baat found that the salt lost 1·85 per cent. at 110°; 3·16, at 130°: 3·67, at 150°; 12·83, at 170°; 28·24, at 182°; 29·24, at 195°; and 29·24, at a red-heat. The salt was found by F. Heeren to be soluble in water—100 parts of water at 16° dissolve 6·06 parts of salt, and at 100°, 6·33 parts; and is insoluble in alcohol. W. C. de Baat gave 2·52 per cent. for the solubility of the potassium salt at 0°; 4·28, at 12°; 6·23, at 20°; and 8·54, at 30°.

R. F. Weinland and J. Alfa prepared crystals of **rubidium dithionate,** by double decomposition with rubidium sulphate and barium dithionate. The crystals are isomorphous with the potassium salt, and J. Piccard said that the axial ratio of the trigonal crystals is $a : c = 1 : 0·6307$, and $\alpha = 108° 56'$. H. Topsöe and C. Christiansen gave for the indices of refraction, $\omega = 1·4556$ and $\epsilon = 1·5041$ for the C-line; $\omega = 1·4574$ and $\epsilon = 1·5078$ for the D-line; and $\omega = 1·4623$ and $\epsilon = 1·5167$ for the F-line. A. Eringhaus and H. Rose found for the index of refraction of rubidium dithionate at about 26°, for lines of wave-length λ in $\mu\mu$:

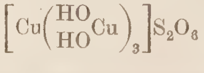
λ . .	718·5	623·9	589·3	491·6	404·7
ω . .	1·45438	1·45688	1·45729	1·46160	1·46850
ε . .	1·47576	1·47867	1·48005	1·48585	1·49508
ε−ω . .	0·02138	0·02179	0·02276	0·02425	0·02658

H. Rose prepared the *hemihydrate*, $Rb_2S_2O_6.\frac{1}{2}H_2O$, but the crystals were not measurable. C. Chabrié prepared **cæsium dithionate** by mixing at 60° soln. of 20·996 grms. of cæsium sulphate, and 17·226 grms. of barium thiosulphate, and evaporating the filtered liquid in vacuo. The colourless hexagonal plates decompose when heated, forming sulphite and sulphate. H. Rose gave for the axial ratio of the hexagonal crystals of $Cs_2S_2O_6$, $a : c=1 : 0·6316$; and said the salt is isomorphous with the dithionates of potassium and rubidium. The optical character is negative. A. Eringhaus and H. Rose found for the index of refraction of cæsium dithionate at about 25° for lines of wave-length λ in $\mu\mu$:

λ . .	718·5	623·9	589·3	513·2	404·7
ω . .	1·51906	1·52184	1·52298	1·52686	1·53659
ε . .	1·53847	1·54211	1·54380	1·54937	1·56404
ε−ω . .	0·02111	0·02027	0·02082	0·02251	0·02745

H. Rose prepared the *hemihydrate*, $Cs_2S_2O_6.\frac{1}{2}H_2O$, in rhombic crystals with the axial ratios $a : b : c=0·8832 : 1 : 0·5058$; the optic axial angle, $2E=50°\ 5'$.

F. Heeren prepared blue, tabular crystals of **cupric dithionate,** $CuS_2O_6.4H_2O$, from the product of the metathetical action of barium dithionate and cupric sulphate soln. K. Klüss evaporated the filtered soln. between 35° and 40°. F. Heeren's analysis indicates that the product is the *tetrahydrate.* J. Grailich, and A. Murmann said that the crystals are triclinic, and resemble the pentahydrate. K. Klüss found that the crystals are stable in air, and lose no water over conc. sulphuric acid. F. Heeren showed that the crystals decrepitate when heated, and then decompose, leaving cupric sulphate as a residue; and K. Klüss, that when the conc. aq. soln. is evaporated on a water-bath between 50° and 55°, sulphur dioxide is evolved. F. Heeren said that the salt is easily soluble in water, and insoluble in alcohol. According to H. Topsöe, and K. Klüss, when the aq. soln. is evaporated spontaneously, or by very gentle heat, dark blue, triclinic plates or prisms of the *pentahydrate*, $CuS_2O_6.5H_2O$, are formed. H. Topsöe found for the axial ratios $a : b : c =0·9527 : 1 : 0·5790$, and $\alpha=105°\ 32\frac{1}{2}'$, $\beta=117°\ 34\frac{1}{2}'$, and $\gamma=65°\ 37'$. The (010)-cleavage is perfect, while the (101)-cleavage is less complete. Measurements were also made by C. F. Rammelsberg, and the crystals measured by A. Handl were probably this salt. The crystals deliquesce is moist air; effloresce in dry air; and lose a mol. of water over sulphuric acid or calcium chloride. J. Thomsen gave −4·87 Cals. for the heat of soln. of the pentahydrate in 400 mols of water at 18°. K. Klüss said that 100 parts of water dissolve 156·2 parts of salt at 18·5°. W. C. de Baat gave 43·82 per cent. for the solubility of the tetrahydrate at 0°; 44·91, at 20°; and 45·51, at 38°. F. Heeren said that the crystals detonate when heated. H. Topsöe found that when the crystals are slowly heated, they decompose at 100°, and at a higher temp., leave a residue of copper sulphate. The conc. soln. gives off sulphur dioxide when evaporated on a water-bath. W. C. de Baat said that the tetrahydrate loses 40·43 per cent. at 95°; 44·09, at 180°; and 46·52, at 185°. K. Klüss obtained a pale blue powder of cupric hexahydroxydithionate, $3CuO.CuS_2O_6.3H_2O$, *i.e.* $3Cu(OH)_2.CuS_2O_6$, by mixing dil. soln. of copper acetate and sodium thiocyanate at 70°, and by treating a soln. of the normal salt and sodium acetate or cupric acetate; and P. Sabatier, by allowing a soln. of the normal salt to act on $4CuO.H_2O$ for a few weeks. A. Werner regarded it as a hexol-salt,



$$\left[\mathrm{Cu}\left(\begin{matrix}\mathrm{HO}\\ \mathrm{HO}\end{matrix}\mathrm{Cu}\right)_3\right]\mathrm{S_2O_6}$$

P. Sabatier's product appeared in pale blue, minute, hexagonal plates. K. Klüss added that this basic salt is insoluble in water, and in soln. of sodium acetate, but traces dissolve in a conc. soln. of copper dithionate. The salt is soluble in dil. acids, in acetic acid, and in dithionic acid. The salt is stable in air, and does not absorb carbon dioxide therefrom. Boiling water gradually transforms it into cupric oxide, and the acid is abstracted by warm water. At 100°, the salt loses traces of water, and at a higher temp., it slowly turns dark green, then dirty green, yellowish-green, and at a dull red-heat it becomes ochre-yellow, forming cupric oxysulphate mixed with a little copper oxide. F. Heeren reported a *hydrate,* $3Cu(OH)_2.CuS_2O_6.H_2O$, or $3CuO.CuS_2O_6.4H_2O$, to be formed by treating a soln. of the normal salt with a little ammonia ; and K. Klüss, by the action of a conc. soln. of copper dithionate on copper hydroxide. The properties of these two basic salts appear to be similar, and P. Sabatier said that this hydrate does not exist.

According to J. S. C. Schweizer, if the basic salt be dissolved in aq. ammonia of sp. gr. 0·945, the liquid dissolves cellulose, makes gun-cotton gelatinous, and does not dissolve starch flour, but, according to J. Schlossberger, makes it swell up. F. Heeren found that when a dil. soln. of copper dithionate is treated with ammonia until the precipitate is dissolved, and the liquid allowed to stand, crystals of **copper tetramminodithionate,** $CuS_2O_6.4NH_3$, are formed ; J. S. C. Schweizer obtained the salt by treating a soln. of copper tetramminosulphate with barium dithionate ; and D. W. Horn, by gradually adding 35 c.c. of aq. ammonia, of sp. gr. 0·9, to a soln. of 8 grms. of copper dithionate in 12 c.c. of water. The salt can be crystallized from aq. ammonia. The azure-blue, rectangular plates or prisms were found by J. S. C. Schweizer to become dark green at 160°, and are decomposed with the loss of ammonia and sulphur dioxide, and the formation of copper sulphate. F. Heeren said that the salt is a little soluble in cold water, forming, according to K. Klüss, a blue basic salt. J. S. C. Schweizer added that the salt is readily soluble in water at 40°, but in the absence of ammonia the salt is hydrolyzed ; at a temp. exceeding 60°, cupric hydroxide is precipitated and ammonium dithionate remains in soln. The soln. is decomposed by hydrochloric acid with the precipitation of a basic chloride. D. W. Horn said that the salt is dissolved by liquid ammonia, forming **copper enneamminodithionate,** $CuS_2O_6.9NH_3$, which decomposes rapidly at ordinary temp., forming the tetrammine. G. T. Morgan and F. H. Burstall prepared **copper bisethylenediaminedithionate,** $[Cu\,en_2]S_2O_6$, in purple-red crystals, by mixing 4·8 grms. of sodium dithionate, 5·0 grms. of copper sulphate, and 2·4 grms. of ethylenediamine in aq. soln., and drying the salt over sulphuric acid. This complex cupric thionate is quite stable in air at the ordinary temp., and on heating it decomposed with blackening at 260°. It is only very sparingly soluble in cold water, but dissolves more readily on warming to form a stable purple soln. Barium chloride and silver nitrate are without action on the hot or cold soln. ; with sodium hydroxide the colour is changed to blue, whereas with mineral acids it is discharged. K. Klüss prepared **ammonium copper dithionate,** $(NH_4)_2S_2O_6.2CuS_2O_6.8H_2O$, from a soln. of the component salts in the molar proportions 1 : 1 or 1 : 2 ; or by adding the necessary quantity of ammonium cupric sulphate to barium dithionate. The filtered soln. furnishes pale blue crystals which, according to A. Fock, are monoclinic prisms with the axial ratios $a : b : c = 0·6874 : 1 : 0·3549$, and $\beta = 95° 30'$. The optic axial angle $2H = 72°$. When heated in a test-tube, some cuprous oxide is formed. W. C. de Baat obtained a curve resembling Fig. 128, for the ternary system $(NH_4)_2S_2O_6$–CuS_2O_6–H_2O, at 30°. The curve *ad* represents the solubility with $CuS_2O_6.4H_2O$ as the solid phase ; *de,* the solubility with the complex ammonium copper dithionate as the solid phase ; and *eb,* the solubility with

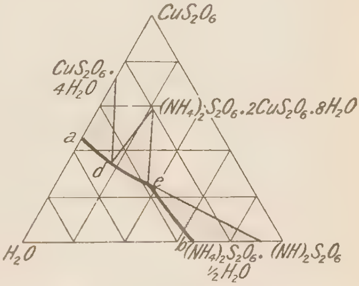

CuS_2O_6
$CuS_2O_6.4H_2O$
$(NH_4)_2S_2O_6.2CuS_2O_6.8H_2O$
a
d
e
b
H_2O
$(NH_4)_2S_2O_6.\frac{1}{2}H_2O$
$(NH)_2S_2O_6$

FIG. 128.—The Ternary System : CuS_2O_6–$(NH_4)_2S_2O_6$–H_2O, at 30° (Diagrammatic).

$(NH_6)_2S_2O_6.\frac{1}{2}H_2O$ as the solid phase ; while *d* and *e* are triple points—2 solids and one soln. The percentage solubilities are :

CuS_2O_6 .	45·51	37·26	*36·19*	36·04	29·70	24·17	10·45	0	per cent.
$(NH_4)_2S_2O_6$	0	16·16	*18·39*	18·50	29·28	38·30	52·62	64·60	,,

F. Heeren prepared **silver dithionate,** $Ag_2S_2O_6.2H_2O$, from a soln. of silver carbonate ; and, added J. S. Stas, the acid should be freshly prepared because when kept it is liable to suffer some decomposition. Moist silver sulphite was found by H. Baubigny to form dithionate when exposed to heat or light. The rhombic, bipyramidal crystals were found by H. Baker to have the axial ratios $a:b:c=0·9884:1:0·5811$. The crystals were also examined by F. Heeren, C. F. Rammelsberg, and V. von Lang. The (110)-cleavage is perfect ; and H. Topsöe and C. Christiansen found the optic axial angles to be $2V=33° 21'$ and $2E=56° 48'$ for the *C*-line ; and $2V=28° 6'$, and $2E=47° 59'$ for the *F*-line. H. Topsöe gave 3·605 for the sp. gr., and P. Groth, 3·620. J. Thomsen gave —10·36 Cals. at 18° for the heat of soln. of the dihydrate in 400 mols of water. H. Topsöe and C. Christiansen found the indices of refraction $\alpha=1·6272$, $\beta=1·6573$, and $\gamma=1·6601$ for the *C*-line, and $\alpha=1·6404$, $\beta=1·6748$, and $\gamma=1·6770$ for the *F*-line. The birefringence is negative. M. Löb and W. Nernst measured the transport number. F. Heeren found that the crystals are stable in air, but blacken when exposed to light ; they decompose when warmed, forming a grey powder ; and with boiling water, some silver sulphide is formed. 100 grms. of water at 16° dissolve 50 grms. of salt. When an aq. soln. is saturated with ammonia, it furnishes small rhombic crystals of **silver tetramminodithionate,** $Ag_2S_2O_6.4NH_3.H_2O$. The salt is coloured grey when exposed to light ; and when heated it gives off water, ammonia, ammonium sulphite, and some free sulphuric acid, and there remains silver sulphate. C. F. Rammelsberg said that the tetrammine dissolves in water without decomposition. K. Kraut obtained what he regarded as **sodium silver dithionate,** $Na_2S_2O_6.Ag_2S_2O_6.6H_2O$, from a soln. of molar proportions of the components. K. Klüss showed that the resulting rhombic, bipyramidal crystals are solid soln. H. Baker gave for the axial ratios $a:b:c=0·9813:1:0·5856$. The (110)-cleavage is perfect.

F. Heeren prepared **calcium dithionate,** $CaS_2O_6.4H_2O$, by adding milk of lime to a soln. of manganese dithionate. The six-sided plates, stable in air, were also prepared by C. Pape, and E. Bichat. H. Topsöe said that the axial ratio of the trigonal crystals is $a:c=1:1·500$, and $\alpha=81° 42'$. The (111)-cleavage is perfect. H. Baumhauer, C. Pape, and L. Sohncke studied the corrosion figures ; and C. Gaudefroy, the dehydration figures. H. Topsöe gave 2·180 for the sp. gr. ; H. Baker, 2·175 at 11° ; and P. Groth, 2·183. V. von Lang studied the thermal conductivity. J. Thomsen found the heat of soln. in 400 mols of water at 18° to be —7·97 Cals. The heat of dilution of calcium dithionate was shown by W. Nernst and W. Orthmann to be positive. H. Topsöe and C. Christiansen found the index of refraction to be $\omega=1·5468$ for the *C*-line ; 1·5496 for the *D*-line ; and 1·5573 for the *F*-line. The birefringence is negative. C. Pape gave 2° 1′ for the optical rotation of the crystals with green-light—soln. are inactive. The crystals were found by C. Pape to effloresce at 78°. W. C. de Baat said that the crystals lose 26·1 per cent. at 110° ; 26·5, at 140° ; 27·1, at 145° ; 27·4, at 165° ; 49·1, at 195° ; and 49·85, at a red-heat. F. Heeren found that 100 grms. of water at 19° dissolve 40·65 grms. of the salt, and 125·0 grms. at 100°. W. C. de Baat found the solubility of the tetrahydrate to be 13·80 per cent. at 0° ; 17·63, at 12° ; 20·25, at 20° ; and 23·29, at 30°. F. Ishikawa and G. Kimura gave for the solubility of calcium dithionate in *S* grms. of anhydrous salt per 100 grms. of soln. :

	0°	10°	20°	30°	50°	70°	90°
S . .	13·86	17·20	20·18	23·12	28·48	33·14	28·04
Sp. gr. .	1·1213	1·1504	1·1772	1·2015	1·2470	1·2900	1·338

The solid phase is $CaS_2O_6.4H_2O$; and the eutectic point occurs with $S=13·40$, and at −2·09°. 2·04 grms. of calcium dithionate in 100 grms. of soln. lowers the f.p. by 0·32°; 5·84 grms., by 0·85°; 9·10 grms., by 1·38°; 9·23 grms., by 1·41°; and 13·40 grms., by 2·09°. F. Heeren said that the salt is insoluble in alcohol; and, according to A. Naumann, insoluble in acetone. F. Heeren prepared **strontium dithionate,** $SrS_2O_6.4H_2O$, in six-sided plates, belonging to the trigonal system, and having, according to C. F. Rammelsberg's calculations from F. Heeren's measurements, $a : c = 1 : 1·5024$, and $\alpha = 81° 47'$. Observations were also made by H. de Sénarmont, and W. G. Hankel and E. Lindenberg. The (111)-cleavage is imperfect. Corrosion figures were observed by H. Baumhauer, and L. Sohncke; and the dehydration figures by C. Gaudefroy. H. Topsöe gave 2·373 for the sp. gr., and P. Groth, 2·348. J. Thomsen found the heat of soln. in 400 mols of water at 18° to be −4·62 Cals. H. Topsöe and C. Christiansen found the indices of refraction to be $\omega = 1·5266$ and $\epsilon = 1·5232$ for the *C*-line; $\omega = 1·5296$ and $\epsilon = 1·5252$ for the *D*-line; and $\omega = 1·5371$ and $\epsilon = 1·5312$ for the *F*-line. A. Fock also gave $\omega = 1·5293$ and $\epsilon = 1·5252$ for the *D*-line. C. Pape gave 1° 6′ for the optical rotatory power, and G. Bodländer, 3° 39′ for yellow-light—aq. soln. are optically inactive. A. Ehringhaus and H. Rose studied the refractive index and dispersion. R. Robl observed no fluorescence with the salt in ultra-violet light. W. G. Hankel and E. Lindenberg studied the piezoelectricity of the crystals. F. Heeren found that the crystals decrepitate when heated, and at a higher temp. decompose leaving a residue of the sulphate. W. C. de Baat observed that the crystals lost 17·18 per cent. at 90°; 40·88, at 110°; 41·23, at 125°; and 42·54, at a red-heat. F. Heeren found that 100 parts of water at 16° dissolve 22·22 parts of salt, and at 100°, 66·67 parts. W. C. de Baat gave 4·51 for the percentage solubility of the tetrahydrate at 0°; 7·37, at 10°; 10·80, at 20°; and 23·29, at 30°. F. Heeren found that the salt is soluble in alcohol.

J. L. Gay Lussac and J. J. Welter, and F. Heeren prepared **barium dithionate,** $BaS_2O_6.2H_2O$, as in the case of the calcium salt. The analyses of J. L. Gay Lussac and J. J. Welter, F. Heeren, and R. H. Ashley agree that the salt is the *dihydrate.* J. C. G. de Marignac found that the monoclinic prismatic crystals have the axial ratios $a : b : c = 0·9343 : 1 : 0·14030$, and $\beta = 110° 37'$. The crystals were also examined by F. A. Walchner, V. von Lang, and C. F. Rammelsberg. The (111)-cleavage is perfect. H. Baker gave 4·536 for the sp. gr., at 13·5°. F. A. H. Schreinemakers and B. C. van B. Walter studied the osmosis of the aq. soln. J. Thomsen gave for the heat of soln. in 400 mols of water at 18°, −6·93 Cals. P. Bary found that the salt is fluorescent when exposed to X-rays or to Becquerel's rays; and V. J. Sihvonen found maxima in the ultra-red spectrum for the wave-length $8·2\mu$, $10·2\mu$, and $18·0\mu$. R. H. Ashley said that the crystals do not effloresce readily in air; and J. L. Gay Lussac and J. J. Welter found the crystals to be stable in air; to decrepitate when heated; and at a higher temp. decompose. F. Ishikawa and G. Kimura found that the dehydration of barium dithionate at different temp. leads directly to the formation of the anhydrous salt; at 90°, a very small amount of barium sulphate is formed. The reaction $BaS_2O_6 = BaSO_4 + SO_2$ is irreversible; it proceeds very slowly at 140°, but is complete after 30 mins. at 700°. W. C. de Baat observed that 11·2 per cent. of water is lost at 110°; 11·8, at 140°; 16·4, at 145°; 28·9, at 165°; and 30·16, at a red-heat. J. Cornog and W. E. Henderson found that *N*-soln. of barium dithionate behave on heating like those of sodium dithionate (*q.v.*). J. L. Gay Lussac and J. J. Welter reported that 100 parts of water at 8·14° dissolve 13·94 parts of salt; F. Heeren gave 24·75 parts of salt at 18°, and 90·9 parts at 100°. H. Baker said that the sat. aq. soln. boils at 102°, and the solubility at this temp. is 100·1 grms. per 100 grms. of water. W. C. de Baat found 7·86 for the percentage solubility of the dihydrate at 0°; 12·45, at 12°; 15·75, at 20°; and 19·86, at 30°. F. Ishikawa and G. Kimera gave for the solubility of barium dithionate in *S* grms. of anhydrous salt per 100 grms. of soln.:

	0°	10°	20°	30°	50°	70°	90°
S . .	7·75	11·56	15·63	19·70	26·91	33·08	38·42
Sp. gr. . .	1·0702	1·1049	1·1430	1·1839	1·2560	1·3240	1·3870

The solid phase is $BaS_2O_6.2H_2O$; and the eutectic point occurs with $S=7·55$, and at $-0·64°$. 2·24 grms. of barium dithionate in 100 grms. of soln. lower the f.p. by 0·240°; 3·98 grms., by 0·340°; 5·70 grms., by 0·480°; 7·55 grms., by 0·640°. F. Heeren said that the salt is insoluble in alcohol; and A. Naumann, insoluble in methyl acetate. R. Otto said that the aq. soln. is reduced by sodium amalgam to sulphite—*vide supra*. F. Heeren, J. C. G. de Marignac, and C. F. Rammelsberg said that below 5° the aq. soln. furnishes crystals of the *tetrahydrate*, $BaS_2O_6.4H_2O$. The former said that the monoclinic prisms have the axial ratios $a:b:c=1·2215:1:1·1272$, and $\beta=94° 16'$. The sp. gr. given by H. Topsöe is 3·142, and by F. W. Clarke, 3·05, at 24·5°. G. N. Wyrouboff gave for the optic axial angle $2V=87° 20'$; and $\beta=1·532$ for the index of refraction for red-light; the bi-refringence is positive. F. Heeren said that the crystals of the tetrahydrate rapidly effloresce, forming the dihydrate; and when heated, the crystals pass into barium sulphate without melting or changing their form. A. Fock and K. Klüss evaporated a soln. of eq. proportions of barium dithionate and chloride, and obtained colourless, prismatic crystals of **barium chlorodithionate,** $BaS_2O_6.BaCl_2.4H_2O$. The triclinic crystals have the axial ratios $a:b:c=0·6720:1:0·6398$, and $\alpha=107° 12'$, $\beta=98° 11'$, and $\gamma=99° 57\frac{1}{2}'$. W. C. de Baat found that the evidence of the formation of ammonium barium dithionate is indefinite. The solubilities at 30° are:

BaS_2O_6 .	19·76	17·20	10·26	6·92	2·75	1·05	0·35	0 per cent.
$(NH_4)_2S_2O_6$.	0	11·00	37·26	40·15	48·45	53·81	58·64	64·60

W. C. de Baat measured the solubility of the dithionates of the three alkaline earths in mixtures of alcohol and water, and found the results could be represented graphically by curves of the type indicated in Fig. 129, where *ab* represents the solubility of the hydrate—$BaS_2O_6.2H_2O$, $SrS_2O_6.4H_2O$, or $CaS_2O_6.4H_2O$—and *bc*, the solubility of the anhydrous salt. In the ternary system, the soln. contained, at 30°:

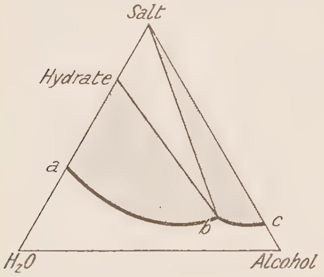


FIG. 129.—Ternary System with Salt, Water, and Alcohol (Diagrammatic).

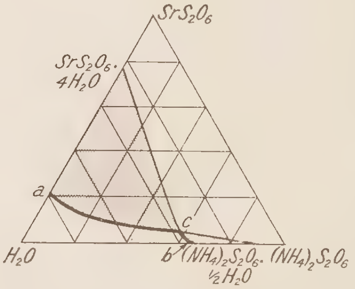


FIG. 130.—Ternary System: $(NH_4)_2S_2O_6$–$Sr_2S_2O_6$–H_2O at 30°.

Alcohol .	0	4·67	16·86	21·36	31·91	61·24	88·69	per cent.
BaS_2O_6 .	19·86	12·74	4·24	2·74	0·86	0·03	0·00	,,
Alcohol .	0	14·48	37·22	60·39	76·13	90·05	98·53	,,
SrS_2O_6 .	14·90	5·40	0·68	0·08	0·0012	0·00	0·00	,,
Alcohol .	0	16·50	40·39	50·96	73·08	82·79	99·80	,,
CaS_2O_6 .	23·29	12·55	3·31	1·39	0·11	0·063	0·00	,,

Ternary systems with pairs of salts in contact with water furnish curves resembling Fig. 130, when no double salt is formed. This is the case, for example, with mixtures of strontium and ammonium dithionates at 30°, where *ac* represents the solubility of the hydrate $SrS_2O_6.4H_2O$; and *bc*, that of the hydrate $(NH_4)_2S_2O_6.\frac{1}{2}H_2O$, where *b* is the triple point with both hydrates (italicized in the Tables) as solid phase, at 30°.

SrS_2O_6 . .	14·90	10·73	2·77	*2·17*	0·98	0	per cent.
$(NH_4)_2S_2O_6$.	0	16·55	56·51	*60·66*	63·73	64·60	,,

Similarly also with

SrS_2O_6	14·90	12·24	*10·09*	5·55	0		per cent.
$Na_2S_2O_6$	0	6·91	*13·06*	14·52	17·32		,,
BaS_2O_6	19·76	17·06	*14·49*	13·23	7·32	0	per cent.
$Na_2S_2O_6$	0	6·36	*13·19*	13·31	14·87	17·32	,,
BaS_2O_6	19·86	20·64	*20·69*	11·74	6·02	0	,,
$K_2S_2O_6$	0	4·16	8·03	8·33	8·49	8·5	,,
BaS_2O_6	19·86	13·37	5·85	1·92	0·90	0	,,
MgS_2O_6	0	7·05	18·91	29·16	34·57	35·24	,,

There is here no evidence of the formation of complex salts, and similar results were obtained at temp. down to 0°. On the other hand, K. Kraut reported **sodium barium dithionate,** $Na_2Ba(S_2O_6)_2.4H_2O$, and H. Schiff, $Na_2Ba(S_2O_6)_2.6H_2O$; but K. Kraut later showed that the product is only a solid soln. of the component salts. G. Bodländer evaporated the filtered soln. obtained after mixing rubidium sulphate with an excess of barium dithionate; and recrystallized the product from hot water. Analyses agree with **rubidium barium dithionate,** $Rb_4Ba(S_2O_6)_3.H_2O$. The white, needle-like crystals are more soluble in hot than in cold water, and the soln. is easily undercooled. 100 c.c. of water at 15° dissolve 10·34 grms. of the salt; an excess of barium dithionate increases, and an excess of rubidium dithionate decreases the solubility.

K. Klüss obtained what he thought to be **beryllium hexahydroxydithionate,** $5BeO.2S_2O_5.14H_2O$, or $3BeO.2BeS_2O_6.14H_2O$, or $3Be(OH)_2.2BeS_2O_6.11H_2O$, by digesting dithionic acid with an excess of freshly precipitated beryllium hydroxide at 30°–35°. The clear soln. on evaporation over sulphuric acid in vacuo, gives a viscid mass which does not crystallize. It is easily soluble in water and absolute alcohol. When heated, water and sulphur dioxide are evolved; at a red-heat, sulphuric acid escapes, and beryllia remains.

F. Heeren obtained six-sided, prismatic crystals of **magnesium dithionate,** $MgS_2O_6.6H_2O$, by double decomposition with magnesium sulphate and barium dithionate. The triclinic crystals were found by H. Topsöe to have the axial ratios $a:b:c=0·6997:1:1·0144$, and $\alpha=89° 32'$, $\beta=118° 10'$, and $\gamma=93° 21'$. The (110)- and (110)-cleavages are perfect, and the (010)-cleavage is clear. The crystals are isomorphous with those of the corresponding salts of zinc, and nickel, but not cadmium. The sp. gr. is 1·666. J. Thomsen gave for the heat of soln. in 400 mols of water at 18°, −2·96 Cals. F. Heeren said that when heated, the salt melts in its water of crystallization, and at a red-heat yields a residue of magnesium sulphate. W. C. de Baat found that 25·55 per cent. is lost at 110°; 29·9, at 125°; 40·9, at 145°; 58·1, at 195°; and 58·5, at a red-heat. F. Heeren found that the aq. soln. can be boiled without decomposition. 100 parts of water dissolve 117·6 parts of salt at 13°; H. Baker said 144·5 parts at 17°. W. C. de Baat found the

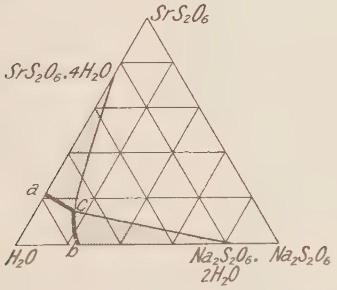


FIG. 131.—Ternary System: $Na_2S_2O_6$–SrS_2O_6–H_2O, at 30°.

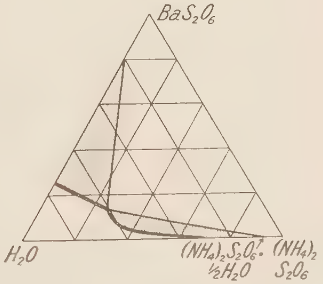


FIG. 132.—Ternary System $(NH_4)_2S_2O_6$–BaS_2O_6–H_2O, at 30°.

percentage solubility to be 31·94 at 0° ; 33·30, at 12° ; 33·91, at 20° ; 35·24, at 30°. H. Schiff, and K. Kraut prepared **barium magnesium dithionate,** $BaMg(S_2O_6)_2.4H_2O$, from a soln. of the component salts. The crystals become anhydrous at 90°. W. C. de Baat obtained no evidence of the formation of this salt, Fig. 131—*vide supra.*

F. Heeren prepared **zinc dithionate,** $ZnS_2O_6.6H_2O$, from the soln. obtained by mixing eq. quantities of barium dithionate and zinc sulphate. A. Fock said that the crystals are triclinic, and H. Topsöe found them to be isomorphous with the magnesium and nickel salts. The sp. gr. is 1·915. J. Thomsen said that the heat of formation $(Zn,O_2,2SO_2,6H_2O)=173·85$ Cals. ; and the heat of soln., in 400 mols of water at 18°, is −2·24 Cals. The crystals have an astringent taste ; they are stable in air ; and freely soluble in water. C. F. Rammelsberg obtained prismatic crystals of what was presumably **zinc tetramminodithionate,** $ZnS_2O_6.4NH_3.H_2O$, by cooling a hot sat. soln. of zinc dithionate in aq. ammonia. The salt is hydrolyzed by water, forming zinc oxide. F. Ephraim and E. Bolle also obtained the same salt, and found that it loses water at 95° when heated in a current of ammonia. The heat of formation is 13 Cals. per mol of ammonia ; and the dissociation temp. is 97°. If the tetrammine is exposed to a current of ammonia for a long time, **zinc pentamminodithionate,** $ZnS_2O_6.5NH_3$, is formed. The heat of formation is 12·1 Cals. per mol of ammonia ; and the dissociation temp., 70°. K. Klüss prepared crystals of **ammonium zinc dithionate,** $5(NH_4)_2S_2O_6.ZnS_2O_6.9H_2O$, from eq. soln. of the component salts. A. Fock recognized two types of crystals—one very similar to those of hexahydrated zinc dithionate, and the other were monoclinic prisms with the axial ratios $a:b:c=2·0597:1:1·2042$, and $\beta=90°\ 52'$. They are probably solid soln. ; they are said to be isomorphous with the corresponding salts of cadmium, manganese, ferrous iron, cobalt and nickel.

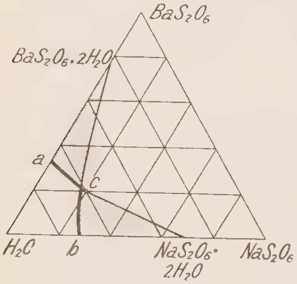


FIG. 133.—Ternary System : $Na_2S_2O_6$–BaS_2O_6–H_2O, at 30°.

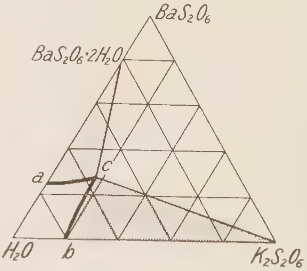


FIG. 134.—Ternary System : $K_2S_2O_6$–BaS_2O_6–H_2O, at 30°.

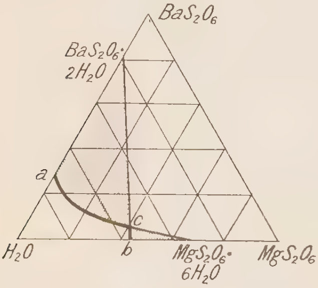


FIG. 135.—Ternary System : BaS_2O_6–MgS_2O_6–H_2O, at 30°.

F. Heeren prepared crystals of **cadmium dithionate,** $CdS_2O_6.6H_2O$, from a soln. of cadmium carbonate in dithionic acid. H. Topsöe said that the triclinic crystals have the axial ratios $a:b:c=1·2030:1:0·9797$, and $\alpha=96°\ 15'$, $\beta=107°\ 52'$, and $\gamma=66°\ 55'$. The (100)-cleavage is perfect, and the (110)-cleavage is clear. The crystals are not isomorphous with the corresponding magnesium, zinc, and manganese salts. The sp. gr. is 2·272. J. Cornog and W. E. Henderson found that N-soln. of cadmium dithionate behave on heating like those of sodium dithionate (*q.v.*). C. F. Rammelsberg found that when dissolved in warm aq. ammonia, and the soln. spontaneously evaporated, crystals of **cadmium tetramminodithionate,** $CdS_2O_6.4NH_3$, are obtained mixed with some cadmium hydroxide and dithionate. The crystals are decomposed by alcohol. K. Klüss prepared **ammonium cadmium**

dithionate, $2(NH_4)_2S_2O_6.CdS_2O_6.4\frac{1}{2}H_2O$, from a soln. obtained by mixing ammonium cadmium sulphate and barium dithionate. The monoclinic plates or prisms are stable in air. A. Fock gave for the axial ratios of the triclinic crystals $a:b:c=1{\cdot}2030:1:0{\cdot}9797$, and $\alpha=96°\ 15'$, $\beta=107°\ 52'$, and $\gamma=66°\ 55'$. The (100)-cleavage is perfect, and the (110)-cleavage clear. The salt is easily soluble in water.

F. Heeren observed that when freshly precipitated mercuric carbonate is digested in dithionic acid, it forms a pale yellow mass which dissolves very slowly; and when a soln. of silver dithionate is shaken with mercury, a white precipitate is formed which blackens when treated with ammonia. According to C. F. Rammelsberg, if an excess of mercuric oxide be digested with dithionic acid, a yellowish-white powder remains on the filter-paper; and K. Klüss obtained **mercuric trioxybisdithionate,** $5HgO.2S_2O_5$, or $3HgO.2HgS_2O_6$, in a similar way. The product was washed with cold water and dried over sulphuric acid. It is also formed when a soln. of mercuric oxide in dithionic acid is treated with alcohol. The compound decomposes when heated, forming mercury, sulphur dioxide, and mercurous and mercuric sulphates. In a sealed tube, the temp. of decomposition is 70°. The substance is also decomposed by acids. C. F. Rammelsberg, and K. Klüss obtained **mercuric dithionate,** $HgS_2O_6.4H_2O$, by digesting freshly precipitated mercuric oxide with an excess of dithionic acid for 8 days at ordinary temp. The large prismatic crystals decompose readily; so does the aq. soln., forming mercurous sulphate and sulphuric acid. C. F. Rammelsberg obtained a soln. of **mercurous dithionate,** $Hg_2S_2O_6$, by dissolving freshly precipitated mercurous oxide in dithionic acid. When the filtered soln. is evaporated, crystals of mercurous dithionate are formed. These, when heated, give off mercury, mercurous sulphate, and free sulphuric acid; they dissolve sparingly in cold water; they are decomposed by hot water becoming black; they are dissolved by nitric acid; and potash-lye extracts mercurous oxide from them.

F. Heeren allowed the filtrate obtained after mixing aluminium sulphate and barium dithionate to evaporate spontaneously, and obtained small crystals which K. Klüss showed were **aluminium dithionate,** $Al_2(S_2O_6)_3.18H_2O$. If the soln. be evaporated in vacuo, the salt decomposes. The colourless plates are very deliquescent; and readily dissolve in water or in absolute alcohol. They melt at about 60° to a colourless liquid, and at the same time they partially decompose. At a higher temp., water and sulphur dioxide are evolved, and at a red-heat, alumina remains. K. Klüss obtained deliquescent crystals of **ammonium aluminium dithionate,** $Al_2(S_2O_6)_3.(NH_4)_2S_2O_6.27H_2O$, from a soln. of the component salts; and A. Fock gave for the axial ratios of the monoclinic crystals $a:b:c=5{\cdot}2672:1:3{\cdot}6620$, $\beta=111°\ 53'$. The crystals are soluble in water.

According to K. Klüss, thallic hydroxide is not attacked by cold dithionic acid, and when heated the thallic compound is reduced, forming thallous sulphate. A. F. G. Werther obtained **thallous dithionate,** $Tl_2S_2O_6$, by the action of dithionic acid on thallous hydroxide, or better, by double decomposition between thallous sulphate and barium dithionate. W. Stortenbeker found that the preparation of thallous dithionate from thallous sulphate and barium dithionate is complicated by the facts that barium and thallium dithionates form anhydrous mixed crystals, and that thallous sulphate and dithionate form a double salt. Either the calculated amounts of the two salts may be taken or else the thallous sulphate may be added in such slight excess that a fresh addition to the filtered soln. causes no further precipitation. The salt is then fractionally crystallized until free from sulphate. The crystals are monoclinic prisms or plates, and, according to A. Fock, have the axial ratios $a:b:c=0{\cdot}9292:1:0{\cdot}3986$, and $\beta=96°\ 58'$; there is no marked cleavage; and the optic axial angle $2E$ is nearly 40° with Na-light. G. N. Wyrouboff found the sp. gr. to be 5·573. According to E. Franke, the eq. conductivity, λ mho, at 25°, is:

v .	32	64	128	256	512	1024
λ .	131·7	141·9	151·7	160·2	166·7	170·6

Thallous dithionate is very soluble in water; K. Klüss said that 100 grms. of water at 18·5° dissolve 41·8 parts of salt. When heated to dull redness, A. F. G. Werther found that the salt loses its sulphur as sulphur dioxide. If ammonia be added to the aq. soln., the liquid on evaporation furnishes small, monoclinic crystals of **thallous hydroxydithionate,** $Tl_2S_2O_6.TlOH.H_2O$. The soln. readily absorbs carbon dioxide from the air. The salt decomposes at 140°–150°. A. Fock, and K. Klüss obtained solid soln. of *lithium thallous dithionates* with Li : Tl=4 : 3, by crystallization from a soln. of the component salts; the monoclinic prisms have the axial ratios $a:b:c=0·8715:1:0·4288$, and $\beta=92° 11'$; similarly with *sodium and thallous dithionates*, where the rhombic crystals had the axial ratios $a:b:c=0·4788:1:0·7931$; while with a soln. containing *potassium and thallous dithionates* in the molar proportion 1 : 1, rhombic plates were obtained with the axial ratios $a:b:c=0·5700:1:1·4547$, and the optic axial angle $2E=113° 50'$. There were also formed solid soln. of *barium and thallous dithionates* with the two salts in the molar proportions 2 : 3 and 1 : 4; and solid soln. of *strontium and thallous dithionates* in rhombic crystals containing 5·53 per cent. of thallous dithionate, and having the axial ratios $a:b:c=0·5674:1:2·7376$ as well as the ternary mixture of potassium, strontium, and thallous dithionates (respectively 10·73, 10·55, and 78·72 per cent.) in rhombic crystals with the axial ratios $a:b:c=0·5914:1:1·3588$. G. N. Wyrouboff obtained soluble crystals of **thallous sulphatodithionate,** $3Tl_2S_2O_6.Tl_2SO_4$. K. Klüss found that thallous and lead dithionates form a series of solid soln.

P. T. Cleve prepared **lanthanum dithionate,** $La_2(S_2O_6)_3.16H_2O$, and with $23H_2O$, as in the case of the aluminium salt. It is soluble in water; so also with **didymium dithionate,** $Di_2(S_2O_6)_3.24H_2O$; H. Topsöe gave for the axial ratio of the hexagonal crystals $a:c=1:1·2965$. G. N. Wyrouboff obtained **cerous dithionate,** $Ce_2(S_2O_6)_3.3H_2O$, and $15H_2O$, while S. Jolin obtained crystals with $24H_2O$. The pentadecahydrate was obtained in triclinic crystals from soln. at 15°–17°. The crystals had the axial ratios $a:b:c=0·5917:1:1·1912$, and $\alpha=81° 26'$, $\beta=105° 21'$, and $\gamma=86° 38'$, and the sp. gr. 2·288. The trihydrate separates above 20° in triclinic crystals with the axial ratios $a:b:c=0·5807:1:1·2030$, and $\alpha=89° 25'$, $\beta=96° 9'$, and $\gamma=96° 18'$, and sp. gr. 2·631. G. T. Morgan and E. Cahen obtained colourless, acicular crystals of the dodecahydrate, $Ce_2(S_2O_6)_3.12H_2O$, by crystallizing the conc. soln. in vacuo over quicklime or potassium hydroxide. C. von Schule prepared **praseodymium dithionate,** $Pr_2(S_2O_6)_3.12H_2O$, in deliquescent crystals, very soluble in water; O. M. Höglund, **erbium dithionate,** $Er_2(S_2O_6)_3.18H_2O$, very soluble in water and alcohol, but insoluble in ether; and P. T. Cleve, non-deliquescent **yttrium dithionate,** $Y_2(S_2O_6)_3.18H_2O$, very soluble in water, sparingly soluble in alcohol, and insoluble in ether. P. B. Sarkar prepared impure **gadolinium dithionate.** P. T. Cleve obtained presumably **thorium dithionate** in soln. by double decomposition of thorium sulphate and barium dithionate, but it decomposed when the soln. was concentrated by evaporation. K. Klüss represented an unstable product he obtained by $Th(S_2O_6)_2.4H_2O$.

J. Bouquet obtained **stannous dithionate** by the action of dithionic acid on freshly precipitated stannous hydroxide; when the soln. is evaporated in vacuo, it decomposes with the separation of stannous sulphide. K. Klüss found that the soln. deposited a basic salt—**stannous heptoxydithionate,** $8SnO.S_2O_5.9H_2O$, or $7SnO.SnS_2O_6.9H_2O$—on evaporation over sulphuric acid in vacuo. F. Heeren obtained **lead dithionate,** $PbS_2O_6.4H_2O$, by the spontaneous evaporation of a soln. of lead carbonate in dithionic acid. P. Marino, and H. C. H. Carpenter obtained no dithionate by the action of sulphur dioxide on lead dioxide. The crystals resemble those of strontium and calcium dithionates. The colourless, doubly refracting, trigonal crystals were found by A. Brezina to have the axial ratio $a:c=1:1·5160$, and $\alpha=81° 19'$. The crystals were also examined by F. Heeren, and R. Brauns. G. N. Wyrouboff thought that the crystals are monoclinic. There is no marked cleavage. H. Baumhauer, and L. Sohncke examined the corrosion figures; and C. Gaudefroy, the dehydration figures. H. Topsöe gave 3·245 for the sp. gr.; H. Baker, 3·259; P. Groth, 3·199; and J. Behr, 3·238. F. Exner mapped the hardness of the surfaces of the faces of the crystals. V. von Lang found the heat conductivity in a direction perpendicular to the principal axis to be rather smaller than it is when parallel with the chief axis. J. Thomsen gave −8·54 Cals. for the heat of soln. of the tetrahydrate in 400 mols of water. F. Klocke, and G. N. Wyrouboff examined the optical anomalies of the crystals. H. Topsöe and C. Christiansen gave for the indices of refraction $\omega=1{\cdot}6295$ and $\epsilon=1{\cdot}6492$ for the *C*-line; $\omega=1{\cdot}6351$ and $\epsilon=1{\cdot}6531$ for the *D*-line; and $\omega=1{\cdot}6481$ and $\epsilon=1{\cdot}6666$ for the *F*-line. C. Pape found the optical rotary power to be 4·09° for the *C*-line, 5·35° for the *D*-line, 7·25° for the *E*-line, and 8·88° for the *F*-line. A. Ehringhaus and H. Rose studied the refraction index and dispersion. J. Dahlen examined the magnetic rotation of the plane of polarization. F. Heeren said that the salt has a sweet yet astringent taste. F. Heeren, and G. Chancel and E. Diacon said that the salt is very soluble in water, and H. Baker said that 100 parts of water at 20·5° dissolve 115·1 parts of salt. Lead dithionate furnishes lead sulphate when calcined. H. C. H. Carpenter found that the aq. soln. is decomposed by sulphur dioxide, forming lead sulphite and dithionic acid. Ammonia in quantity insufficient to precipitate all the salt was said by F. Heeren to furnish acicular crystals of **lead oxydithionate,** $PbO.PbS_2O_6.2H_2O$; and with more ammonia, the decahydrated basic salt. R. F. Weinland and R. Stroh obtained **lead dihydroxydithionate,** $[Pb_2(OH)_2]S_2O_6$, in lustrous needles by double decomposition of a dithionate and the corresponding lead perchlorate; and similarly also with **lead tetrahydroxydithionate,** $[Pb_3(OH)_4]S_2O_6$, which appears as a colourless crystalline precipitate. Solid soln. of *lead and strontium dithionates* were examined by H. de Sénarmont, C. F. Rammelsberg, G. Bodländer, H. Ambronn, G. Tammann and A. Sworykin; and A. Fock gave for the refractive indices of mixtures with

$PbS_2O_6.4H_2O$.	0	6·5	17·9	21·0	45·0	73·1	86·4	100 per cent.
ω . . .	1·5296	1·5372	1·5479	1·5517	1·5770	1·6064	1·6202	1·6351
ϵ . . .	1·5252	1·5334	1·5477	1·5521	1·5826	1·6182	1·6352	1·6531

L. Vanino and F. Mussgnug were unable to prepare normal **bismuth dithionate,** $Bi_2(S_2O_6)_3$, by the action of sodium dithionate on a bismuth mannitol soln. K. Klüss treated bismuth hydroxide with dithionic acid, and obtained **bismuthyl dithionate,** $(BiO)_2S_2O_6.5H_2O$, as a white mass almost insoluble in water, but decomposed by that menstruum, forming the basic salt $Bi_2O_3(BiO)_2S_2O_6.5H_2O$—**bismuthyl oxydithionate** in monoclinic crystals which, according to A. Fock, have the axial ratios $a:b:c=0{\cdot}543:1:$—, and $\beta=116°\,45'$. The (010)-cleavage is complete. Both salts are soluble in dil. acids. E. J. Bevan observed that if an aq. soln. of barium dithionate be treated with vanadyl sulphate, and the blue filtrate concentrated in vacuo over conc. sulphuric acid, crystals of **vanadyl dithionate,** $(VO_2)_2S_2O_6$, are formed. If the concentration be continued after the appearance of these crystals, decomposition sets in, sulphur dioxide is given off, and vanadyl sulphate remains. This decomposition prevents the separation of the salt of a high degree of purity.

K. Klüss, and A. Fock digested chromic hydroxide with an excess of dithionic acid and obtained a bluish-violet soln., which when slowly evaporated furnishes small, octahedral or tabular, violet crystals of **chromic dithionate,** $Cr_2(S_2O_6)_3.18H_2O$, and a similar soln. is obtained by mixing barium dithionate with chromic sulphate. The salt is easily soluble in water and alcohol. If dithionic acid be treated with an excess of chromic hydroxide, the green soln. appears red in transmitted light, and when evaporated in vacuo furnishes a very hygroscopic mass of **chromic oxydithionate,** $3Cr_2O_3.4S_2O_5.24H_2O$. The same product is precipitated when the green soln. is treated with alcohol or ether.

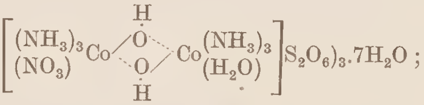
S. M. Jörgensen prepared **chromic hydroxypentamminodithionate,** $[Cr(NH_3)_5(OH)](S_2O_6).2H_2O$; P. Pfeiffer and R. Stern, **chromic *cis*-hydroxyaquobisethylenediaminedithionate,** $[Cr\ en_2(H_2O)(OH)]S_2O_6$; and P. Pfeiffer and R. Prade, **chromic *trans*-hydroxyaquobisethylenediaminedithionate**; O. T. Christensen prepared *xanthochromic dithionate,* or **chromic nitritopentamminodithionate,** $[Cr(NH_3)_5(NO_2)]S_2O_6.H_2O$, in yellow, prismatic crystals, by treating a soluble salt of the series with sodium dithionate. The salt is insoluble in cold water, and it loses its water of hydration at 100°. S. M. Jörgensen obtained carmine-red, six-sided, rhombic crystals of *purpureochromic dithionate* or **chromic pentammino-chlorodithionate,** $[Cr(NH_3)_5Cl]S_2O_6$, by adding sodium dithionate to a chloride of this series of salts. The salt is sparingly soluble in cold water. A. Werner and J. V. Dubsky prepared **chromic dihydroxydiaquodiamminodithionate,** $[Cr(NH_3)_2(H_2O)_2(OH)_2]S_2O_6.H_2O$, as a lilac-coloured, crystalline powder by adding sodium dithionate to a freshly prepared aq. soln. of the bromide. P. Pfeiffer and T. G. Lando prepared deep violet needles of **chromic *cis*-dichlorobisethylenediaminodithionate,** $[Cr(NH_2.CH_2.CH_2.NH_2)_2Cl_2]S_2O_6$, in a similar manner. P. Pfeiffer and A. Koch prepared **chromic *trans*-dichlorobisethylendiaminedithionate.** P. Pfeiffer and A. Trieschmann also obtained **chromic *cis*-dibromobisethylenediaminodithionate,** and also **chromic *trans*-dibromobisethylenediaminodithionate.** S. M. Jörgensen used a similar process in preparing carmine-red, rhombic prisms of *rhodochromic dithionate,* or **chromic decamminohydroxydithionate,** $[Cr_2(OH)(NH_3)_{10}]_2(S_2O_6)_5.2H_2O$, or $[(NH_3)_5Cr\ .\ .\ .\ O(H)—Cr(NH_3)_5]_2(S_2O_6)_5.2H_2O$, almost insoluble in cold water; it loses its water of hydration over sulphuric acid, and decomposes at 100°. S. M. Jörgensen made **chromic decamminodihydroxydithionate,** $[Cr_2(OH)(NH_3)_{10}]_2(S_2O_6)_2.(OH).H_2O$, in pale blue scales, by adding ammonium carbonate and sodium dithionate to a cold sat. soln. of the thiocyanate. The salt is insoluble in water, dil. aq. ammonia, and soda-lye. S. M. Jörgensen obtained *erythrochromic dithionate,* or **chromic pentamminoxydithionate,** $[Cr_2O(NH_3)_{10}](S_2O_6)_2.3H_2O$, in dark violet-red needles, by the action of sodium dithionate on the nitrate. It is soluble in cold water acidified with hydrochloric, hydrobromic, or nitric acid. It loses 2 mols. each of ammonia and water at 100°. P. Pfeiffer and W. Vorster obtained **chromic hexaethylenediaminohexahydroxydithionate,** $[Cr_4(OH)_6(NH_2.CH_2.CH_2.NH_2)_6](S_2O_6)_3.7H_2O$, by the action of sodium dithionate on the chloride of the series.

K. Klüss found that normal **uranyl dithionate,** $(UO_2)S_2O_6$, the soln. obtained from uranyl sulphate and barium dithionate, is not stable, but decomposes over sulphuric acid in vacuo, forming sulphur dioxide and uranyl sulphate. The green soln. of uranous hydroxide in dithionic acid contains **uranous dithionate,** but it decomposes into sulphur dioxide, etc., when allowed to stand over sulphuric acid in vacuo. A series of basic salts—**uranous oxydithionates**—of indefinite composition is produced by mixing soln. of sodium dithionate and uranium tetrachloride, with very dil. soln., $8UO_2.S_2O_5.21H_2O$; with conc. soln., at ordinary temp. $7UO_2.S_2O_5.8H_2O$, is produced; and with warm conc. soln., $6UO_2.S_2O_5.10H_2O$.

J. L. Gay Lussac and J. J. Welter prepared **manganese dithionate,** presumably MnS_2O_6, by the action of sulphur dioxide on water holding manganese dioxide in suspension—*vide supra,* dithionic acid. H. C. H. Carpenter obtained good yields by using manganese sesquioxide. A soln. of the salt is also obtained by double decomposition between manganese sulphate and barium dithionate. If the aq. soln. be spontaneously evaporated, K. Kraut said that rhombic crystals of the *trihydrate,* $MnS_2O_6.3H_2O$, are formed with the axial ratios $a:b:c$ =0·4906 : 1 : 0·5562. J. C. G. de Marignac obtained rose-coloured, triclinic crystals of the *hexahydrate,* $MnS_2O_6.6H_2O$, and he gave for the axial ratios $a:b:c$ =0·6940 : 1 : 1·0307, and α=86° 32′, β=117° 24′, and γ=95° 4′—the (110)- and (110)-cleavages are perfect, and the (010)-cleavage is good. The sp. gr. is 1·757. J. Thomsen gave for the heat of formation $(Mn,O_2,2SO_2,6H_2O)$=188·6 Cals.; $Mn(OH)_2+H_2S_2O_6=MnS_2O_6aq.$+22·78 Cals.; and for the heat of soln. in 400 mols of water at 18°, −1·93 Cals. The crystals effloresce in air; and form manganese sulphate at a dull red-heat. K. Klüss prepared **ammonium manganese dithionate,** $9(NH_4)_2S_2O_6.2MnS_2O_6.16\frac{1}{2}H_2O$, from a soln. of the component salts. The crystals are said to be isomorphous with those of the zinc salt; and A. Fock gave for the axial ratios of the monoclinic crystals $a:b:c=2\cdot1289:1:1\cdot2173$, and $\beta=91°\ 19'$.

F. Heeren prepared **ferrous dithionate,** $FeS_2O_6.5H_2O$, by the action of ferrous sulphate on the calculated amount of barium dithionate, and allowing the filtrate to evaporate, first at a gentle heat, and then spontaneously. The oblique rhombic prisms have the colour and taste of ferrous sulphate. The crystals become brown on exposure to air, and when heated, they leave a residue of ferrous sulphate. K. Klüss said that the salt is heptahydrated, and that 100 parts of water at 18·5° dissolve 169·5 parts of salt. F. Heeren said that the salt is not soluble in alcohol; and that the aq. soln. furnishes ferrous sulphate when boiled. K. Klüss prepared **ammonium ferrous dithionate,** $3(NH_4)_2S_2O_6.FeS_2O_6.6H_2O$, from a soln. of the component salts, and found that the monoclinic prisms have the axial ratios $a:b:c=2\cdot0564:1:1\cdot1907$, and $\beta=90°\ 51'$; the optic axial angle is $2H=72°$ for Na-light. The crystals are probably isomorphous mixtures. He also obtained crystals of $9(NH_4)_2S_2O_6.2FeS_2O_6.16\frac{1}{2}H_2O$. F. Heeren reported that an aq. soln. of dithionic acid dissolves a small amount of freshly precipitated ferric hydroxide; and it unites with the oxide, forming a reddish-brown powder—**ferric oxydithionate,** $8Fe_2O_3.S_2O_5.20H_2O$—which is insoluble in water or alcohol; slightly soluble in dithionic acid; and easily soluble in hydrochloric acid. K. Klüss said that the salt is tetradecahydrated, and he likewise obtained $3Fe_2O_3.S_2O_5.8H_2O$, insoluble in water, but soluble in acids.

F. Heeren made **cobalt dithionate,** $CoS_2O_6.8H_2O$, by evaporating, at a gentle heat, the filtrate from a mixture of soln. of barium dithionate and cobalt sulphate. U. Antony and E. Manasse said that the dithionate is not produced by the action of sulphur dioxide on cobalt sulphate. H. Topsöe said that the dark red triclinic crystals of the *octohydrate* are triclinic with the axial ratios $a:b:c=1\cdot1518:1:1\cdot1230$, and $\alpha=108°\ 14'$, $\beta=85°\ 12'$, and $\gamma=106°\ 4'$. The (001)-cleavage is perfect, and the (010)-cleavage distinct. The sp. gr. is 1·8155. K. Klüss found that rose-red crystals of the *hexahydrate* are precipitated by alcohol from aq. soln. The octohydrate effloresces in dry air; and 100 parts of water at 19° dissolve 204 parts of salt. K. Klüss obtained monoclinic crystals of **ammonium cobalt dithionate,** $9(NH_4)_2S_2O_6.2CoS_2O_6.16\frac{1}{2}H_2O$, from a soln. of the component salt; the crystals of the solid soln. have the axial ratios $a:b:c=2\cdot0594:1:1\cdot2045$, and $\beta=90°\ 54'$; and the optic axial angle $2H=74\frac{1}{2}°$ for Na-light. S. M. Jörgensen obtained **cobalt pentamminohydroxydithionate,** $[Co(NH_3)_5(OH)]S_2O_6.2H_2O$, by boiling 5 grms. of cobalt pentamminonitratonitrate with 70 c.c. of aq. ammonia, adding 6 grms. of sodium dithionate to the filtered soln., concentrating the liquid to 10 c.c. and adding a few drops of alcohol. Carmine-red rhombic or monoclinic, octahedral crystals are precipitated. The salt forms a violet-red soln. with water; though sparingly soluble in water, it is readily soluble in dil. hydrochloric acid; it drives ammonia from ammonium salts; and it loses 2 mols. of water at 100°. C. F. Rammelsberg obtained a salt, $Co_2O_3.2S_2O_5.10NH_3$, thought to be this compound. A. Werner prepared **cobalt diamminodipyridinodihydroxydithionate,** $[Co(NH_3)_2(C_5H_5N)_2(OH)_2]_2(S_2O_6)_3.2H_2O$, in brown, sparingly soluble crystals by adding sodium dithionate to the chloride of the series, also violet, sparingly soluble in crystals of **cobalt tetramminoaquohydroxydithionate,** $[Co(NH_3)_4(H_2O)(OH)]S_2O_6.H_2O$, from the bromide of the series and sodium dithionate. By treating the *cis*-nitrate of cobalt diethyleneamineaquohydroxide in analogous manner, A. Werner prepared violet-red needles of **cobalt *cis*-diethylenediaminoaquohydroxydithionate,** $[Co(NH_2.CH_2.CH_2.NH_2)_2(H_2O)(OH)]S_2O_6$, almost insoluble in water, and soluble in dil. acetic acid or dil. alkali-lye. Likewise also the *trans*-salt furnishes **cobalt *trans*-diethylenediamine-aquohydroxydithionate,** $[Co(NH_2.CH_2.CH_2.NH_2)_2(H_2O)(OH)]S_2O_6$. Large reddish-brown crystals of **cobalt diamminodipyridinoaquo-hydroxydithionate,** $[Co(NH_3)_2(C_5H_5N)_2(H_2O)(OH)]S_2O_6$, were formed in an analogous way. S. M. Jörgensen prepared **cobalt pentamminonitratodithionate,** $[Co(NH_3)_5(NO_3)]S_2O_6.H_2O$, in a similar manner. The red needles are sparingly soluble in cold water, and freely soluble in hot water when they are hydrolyzed to the pentamminoaquo-salt. Hydrochloric and nitric acids convert the dithionate respectively into the chloride and nitrate. He also made violet, rectangular prisms of **cobalt pentamminochlorodithionate,** $[Co(NH_3)_5Cl]S_2O_6$; and carmine-red, dichroic crystals of **cobalt bisethylenediaminoamminochlorodithionate,** $[Co(NH_2.CH_2.CH_2.NH_2)_2(NH_3)Cl]S_2O_6$. For **cobalt diazidobisethylenediaminedithionate,** and **cobalt diazidotetramminodithionate,** *vide* the azides. A. Werner treated a soln. of cobalt pentamminohydroxydithionate with carbon dioxide, and obtained brick-red crystals of **cobalt pentamminohydrocarbonatodithionate,** $[Co(NH_3)_5(HCO_3)]S_2O_6$; brick-red, sparingly soluble needles of **cobalt diethylenediaminodinitritodithionate,** $[Co(NH_2.CH_2.CH_2.NH_2)_2(NO_2)_2]_2S_2O_6$; **cobalt** cis-**tetramminochlorodithionate,** $[Co(NH_3)_4Cl_2]_2S_2O_6$; A. Werner and A. Fröhlich also made **cobalt** *cis*-**dipropylenediaminodichlorodithionate,** $[Co(NH_3.CH_2.CH_2.CH_2.NH_2)_2Cl_2]_2S_2O_6$; likewise also with **cobalt** *trans*-**dipropylenediaminodichlorodithionate,** $[Co(NH_2.CH_2.CH_2.NH_2)_2Cl_2]_2S_2O_6$. S. M. Jörgensen obtained carmine-red rhomboidal plates of **cobalt tetramminocarbonatodithionate,** $[Co(NH_3)_4(CO_3)]_2S_2O_6$; also chocolate-brown needles of **cobalt hexamminoxydiaquohydroxydithionate,** $[(NH_3)_2(H_2O)_2.Co(OH).O.Co(NH_3)_4]_2(S_2O_{63}.2H_2O$, also dark violet crystals of **cobalt dodecamminohexahydroxydithionate,** $[Co_4(OH)_6(NH_3)_{12}]$-$(S_2O_6)_3.4H_2O$; dark red aggregates of needles and prisms of **cobalt hexamminotrihydroxydithionate,** $[Co_2(OH)_3(NH_3)_6]_2(S_2O_6)_3.H_2O$; pale violet scales of **cobalt hexamminotrinitratoaquodihydroxydithionate,**



$$\left[\begin{matrix}(NH_3)_3\\(NO_3)\end{matrix}Co\begin{matrix}\overset{H}{O}\\\underset{H}{O}\end{matrix}Co\begin{matrix}(NH_3)_3\\(H_2O)\end{matrix}\right]S_2O_6)_3.7H_2O;$$

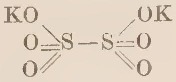
and pale violet needles of **cobalt octamminodihydroxydithionate,** $[Co_2(OH)_2(NH_3)_8]$-$(S_2O_6)_2.2H_2O$. A. Werner and G. Jantsch prepared a pale bluish-red powder of **cobalt tetraethylendiaminediaquotetrahydroxydithionate,** $[Co_3(OH)_4(NH_2.CH_2.CH_2.NH_2)_4(H_2O)_2](S_2O_6)_2.2H_2O$; A. Werner, raspberry-red plates of **cobalt octamminoamidohydroxydithionate,** $[Co_2(NH_2)(OH)(NH_3)_8](S_2O_6)_2.2H_2O$; and a rose-red crystalline powder of **cobalt decamminoamidodithionate,** $[Co_2(NH_2)(NH_3)_{10}]_2(S_2O_6)_5.6H_2O$.

C. F. Rammelsberg prepared **nickel dithionate,** $NiS_2O_6.6H_2O$, by evaporating the filtrate from mixed soln. of barium dithionate and nickel sulphate. H. Topsöe found that the green, triclinic prisms have the axial ratios $a:b:c=0·6968:1:1·0184$, and $\alpha=89° 29'$, $\beta=118° 15\frac{1}{2}'$, and $\gamma=93° 37'$. The (110)- and (110)-cleavages are perfect, and the (010)-cleavage distinct. The sp. gr. is 1·908. C. F. Rammelsberg said that the salt decomposes into sulphur dioxide and nickel sulphate when heated. When the aq. soln. is treated with ammonia, violet-blue plates of **nickel hexamminodithionate,** $NiS_2O_6.6NH_3$, are formed. When heated, ammonia, and ammonium sulphite and sulphate are given off, and nickel sulphide and sulphate remains. The hexammine is decomposed by water with the separation of nickel hydroxide. W. Peters found that the hexammine loses 2 mols. of ammonia at 100°. H. Franzen and O. von Meyer prepared **nickel trihydrazinodithionate,** $NiS_2O_6.3N_2H_4$, by treating a soln. of nickel dithionate with ammonia, and then with hydrazine. The reddish-violet crystals soon decompose; they are soluble in aq. ammonia. K. Klüss prepared **ammonium nickel dithionate,** $9(NH_4)_2S_2O_6.2NiS_2O_6.16\frac{1}{2}H_2O$, from a soln. of the component salts. The product is a solid soln. or isomorphous mixture. The green tabular or prismatic crystals belong to the monoclinic system and have the axial ratios $a:b:c=2·0643:1:1·2077$, and $\beta=90° 56'$, and the optic axial angle $2H=74\frac{1}{2}°$ for Na-light.

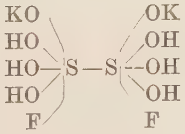
S. G. Hedin obtained a complex salt of **platinous dithionate** and pyridine, $[Pt(C_5H_5N)_4]S_2O_6.nH_2O$, from the sulphate and barium dithionate. The needle-like crystals rapidly effloresce in air. U. Antony and A. Lucchesi observed that

ruthenious dithionate, RuS_2O_6, is produced when sulphur dioxide is passed into a soln. of ruthenium sulphate; it is very soluble in water and is precipitated from its aq. soln. by alcohol as a yellowish-white powder soluble in acids without alteration. On evaporating its aq. soln. at the ordinary temp. over a desiccating substance, ruthenious dithionate is deposited as a pale yellow mass of radiating fibres, composed of optically negative crystals, which are too small to admit their system being determined. On warming with potassium permanganate soln., it is readily oxidized to sulphate and sulphuric acid, the oxidation being more energetic on boiling, and in this case some perruthenic acid, easily recognizable by its odour, is formed. It is also oxidized by the continued action of chlorine, bromine, nitrohydrochloric acid, hydrochloric acid and potassium chlorate, or nitric acid. The formation of ruthenious dithionate by the action of sulphur dioxide on the sulphate comprises two distinct phases; the ruthenic sulphate being first reduced to the ruthenious compound, and sulphur dioxide being subsequently taken up directly by the ruthenious sulphate.

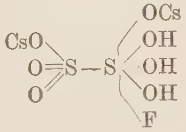
R. F. Weinland and J. Alfa[2] prepared crystals of **potassium difluodithionate,** $K_2S_2O_5F_2.3H_2O$, from a warm, sat. soln. of potassium dithionate in hydrofluoric acid. It is very unstable, and when exposed to air, it quickly decomposes with the evolution of water and hydrofluoric acid, leaving a residue of potassium dithionate; when heated, the salt gives off water and hydrofluoric acid, then sulphur dioxide, leaving a residue of potassium sulphate. He also obtained **rubidium difluodithionate,** $Rb_2S_2O_5F_2.3H_2O$, in all respects like the potassium salt; and **cæsium hydroxyfluodithionate,** $Cs_2S_2O_5(OH)F.H_2O$, was obtained by saturating warm hydrofluoric acid with cæsium dithionate, and cooling. The small, colourless prisms of the cæsium salt are more stable than potassium difluodithionate, but the two salts are similar in other respects. They were unable to prepare *ammonium difluodithionate*, and *sodium difluodithionate*. The supposed constitutions are represented by the graphic formulæ:



$K_2S_2O_6$



$K_2S_2O_5F_2.3H_2O$



$Cs_2S_2O_5(OH)F.H_2O$

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§ 42. Trithionic Acid and the Trithionates

In 1840, C. Langlois[1] in a paper: *Sur un novel oxacide du soufre l'acide hyposulfureux libre*, described the preparation of what he called *sulphhyposulfate de potasse*, that is, sulphated dithionate of potassium, or potassium trithionate, by the action of sulphur on potassium hydrosulphite: $6KHSO_3+2S=2K_2S_3O_6+K_2S_2O_3+3H_2O$. He said:

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ib., (2), **20**. 436, 1873; *Compt. Rend.*, **77**. 1189, 1873; P. Bary, *ib.*, **130**. 776, 1900; G. Bodländer, *Ber.*, **23**. 684, 1890; *Chem. Ztg.*, **14**. 1140, 1890; *Ueber das optische Drehungsvermögen isomorpher Mischung aus des Dithionaten des Blei und des Strontiums*, Breslau, 1882; A. Handl, *Sitzber. Akad. Wien*, **27**. 171, 1857; A. Brezina, *ib.*, **64**. 289, 1871; A. Brio, *ib.*, **55**. 145, 1867; V. von Lang, *ib.*, **37**. 382, 1859; **45**. 28, 1862; **54**. 172, 1866; **102**. 845, 1893; J. Grailich and V. von Lang, *ib.*, **27**. 19, 1857; A. Murmann, *ib.*, **27**. 171, 1857; C. S. Weiss, *ib.*, **37**. 372, 1859; J. Cornog and W. E. Henderson, *Journ. Amer. Chem. Soc.*, **46**. 1978, 1924; C. von Schule, *Zeit. anorg. Chem.*, **18**. 361, 1898; M. L. Huggins and G. Frank, *Phys. Rev.*, (2), **31**. 916, 1928; O. M. Höglund, *Bull. Soc. Chim.*, (2), **18**. 193, 1872; G. T. Morgan and E. Cahen, *Journ. Chem. Soc.*, **91**. 475, 1907; P. R. Ray, *Journ. 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> I first prepare some potassium hydrosulphite by passing a current of sulphur dioxide into a soln. of purified potassium carbonate ; the liquid is saturated when the evolution of carbon dioxide ceases, and the sulphur dioxide escapes *en grande quantité*. The liquid then contains many crystals of potassium hydrosulphite, and no sulphate if the sulphur dioxide was well washed before it passed into the potassium carbonate. The liquid and crystals are mixed with flowers of sulphur, and slightly warmed on a sand-bath ; if the temp. be too high, the trithionate will decompose as it is formed. In three or four days, the sulphite is usually transformed into trithionate ; during the reaction, some sulphur dioxide is given off, and a little sulphate is formed. The yellow colour of the liquid disappears as soon as the formation of the new salt is completed, and this is *un signe certain* that the reaction is ended. The liquid is filtered while hot, and it becomes turbid on cooling by producing crystals of the trithionate and a little sulphur. To purify the crystals from the sulphur, and a little potassium sulphate, they are dissolved at a gentle heat by the smallest possible quantity of distilled water. The filtered soln. is no longer turbid, and it soon deposits *très beaux cristaux prismatiques*.

Both C. Langlois, and F. Kessler said that in order to prepare an aq. soln. of trithionic acid, the potassium salt is treated with an excess of hydrofluosilicic acid ; and baryta water is added to the filtered liquid to precipitate the excess of hydrofluosilicic acid. The soln. of barium trithionate is then treated with sulphuric acid, and the filtered liquid is an aq. soln. of **trithionic acid,** $H_2S_3O_6$, which is concentrated by evaporation over conc. sulphuric acid in vacuo. Neither trithionic acid nor **trithionic anhydride,** S_3O_5, has been isolated. The acid slowly decomposes at ordinary temp. with the separation of sulphur, the evolution of sulphur dioxide, and the formation of sulphuric acid : $H_2S_3O_6=H_2SO_4+SO_2+S$. Even when the acid is concentrated at 0° some decomposition occurs, and at 80°, on a water-bath, the decomposition is rapid. M. J. Fordos and A. Gélis said that the soln. is more stable in the presence of acids. H. Debus found that 24 hrs. after the preparation of the soln. of trithionic acid, the liquid had acquired the odour of sulphur dioxide, and a precipitate of sulphur had formed. At ordinary temp., trithionic acid is slowly decomposing, but after several weeks some undecomposed acid can be detected in the liquid. The sulphur does not all separate in the free state during the decomposition: $H_2S_3O_6=H_2SO_4+SO_2+S$—a portion unites with the undecomposed trithionic acid to form pentathionic and probably also tetrathionic acid. No pentathionic acid could be detected two days after the preparation of the trithionic acid, but after the lapse of 14 days, considerable quantities of pentathionic and sulphuric acids could be detected in the liquid : $3H_2S_3O_6=2H_2SO_4+2SO_2+H_2S_5O_6$. Similarly also with potassium trithionate a clear neutral soln. of a gram of this salt in 10 c.c. of water gave no reaction with ammoniacal soln. of silver nitrate, or with a soln. of potassium hydroxide, but after standing 24 hrs., the soln. had acquired an acidic reaction without the separation of sulphur : $2K_2S_3O_6=K_2S_4O_6+K_2SO_4+SO_2$—no pentathionate could be detected at this stage of the reaction. Six days after the preparation of the soln., potassium sulphate and sulphurous acid were found in abundance, and comparatively large quantities of potassium pentathionate were detected by means of an ammoniacal soln. of silver nitrate, and of potassium hydroxide, respectively. It follows, therefore, that an aq. soln. of potassium trithionate decomposes at 18° slowly into potassium sulphate, sulphurous acid, and sulphur, but the latter is not set free, as it enters into combination with potassium trithionate, forming tetra- and penta-thionate respectively—$3K_2S_3O_6=2K_2SO_4+2SO_2+K_2S_5O_6$. A soln. of one of the three salts, potassium penta-, tetra-, or tri-thionate, will contain, if left to itself for some time, all three salts. A. Kurtenacker and M. Kaufmann represented the reaction $S_3O_6''+H_2O=S_2O_3''+SO_4''+2H^{\cdot}$, and $S_2O_3''+S_3O_6''+H^{\cdot}=S_4O_6''+HSO_3'$. Sulphur is not precipitated, and only a little pentathionate is formed. This occurs at a later stage of the reaction, $5S_2O_3''+6H^{\cdot}=2S_5O_6''+3H_2O$. In acidic soln. the decomposition is more rapid, and a third reaction occurs, $S_2O_3''+H^{\cdot}=HSO_3'+S$. J. Pelouze said that the boiling soln. of potassium trithionate decomposes into potassium sulphite, sulphur dioxide, and sulphur. A. Hornig observed that soln. of trithionates are hydrolyzed, forming sulphate, thiosulphate, and hydrogen ions.

Returning to the preparation of potassium trithionate, J. Pelouze said that the formation of potassium sulphate during the operation is due to the decomposition of the thiosulphate, one of the products of the reaction. C. Saintpierre found that if a dil. soln. of potassium hydrosulphite be heated in a sealed tube on a water-bath, sulphur, and potassium trithionate and sulphate are formed, but no other sulphur compound: $10KHSO_3=5K_2SO_4+H_2S_3O_6+2S+4H_2O$. The liquid first becomes yellow, presumably owing to the formation of sulphur, so that here again, as C. Langlois showed, the trithionate is produced by the action of sulphur on the hydrosulphite. Since sulphur dioxide acts on potassium thiosulphate to form the trithionate, it follows that the action of sulphur on potassium hydrosulphite proceeds in two stages: $3K_2S_2O_6+3S=2K_2S_2O_3+3SO_2+K_2S_2O_6$; and $2K_2S_2O_3+3SO_2=2K_2S_3O_6+S$. A trithionate is produced by the action of sulphur dioxide on a mixed soln. of potassium sulphide and hydrosulphite, $K_2S+4KHSO_3+4SO_2=3K_2S_3O_6+2H_2O$, as shown by G. Chancel and E. Diacon.

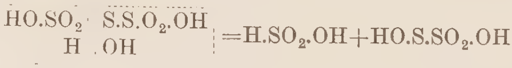
E. Mathieu-Plessy observed that potassium trithionate is formed by the action of sulphur dioxide on a conc. soln. of potassium thiosulphate: $2K_2S_2O_3+3SO_2=2K_2S_3O_6+S$. H. Baker added that with sodium thiosulphate no trithionate but only crystals of the thiosulphate are formed. A. Villiers said that the reaction should be represented: $2Na_2S_2O_3+3SO_2=Na_2S_4O_6+Na_2S_3O_6$. H. Debus showed that E. Mathieu-Plessy's equation cannot be right because the final products of the action are potassium trithionate as the main product, while sulphur and potassium tetra- and penta-thionates are also formed: $6K_2S_2O_3+9SO_2=K_2S_5O_6+K_2S_4O_6+4K_2S_3O_6$, actually less penta- and tetra-thionates and more trithionate are formed on account of the formation of sulphur—*vide supra*, thiosulphuric acid. W. Feld, and F. Raschig studied the reaction. H. Hertlein added that with an excess of sulphur dioxide, no polythionate is formed. E. Josephy and E. H. Riesenfeld observed that the reaction between potassium thiosulphate and sulphur dioxide gives potassium trithionate; with aniline, aniline tetrathionate. B. Rathke showed that the trithionate is produced if a mixture of potassium thiosulphate and hydrosulphite be crystallized together: $2K_2S_2O_3+3SO_2=2K_2S_3O_4+S$; M. J. Fordos and A. Gélis said that the trithionate is produced by evaporating a soln. of zinc in sulphuric acid through the intermediate formation of the dithionate: $2ZnS_2O_3=ZnS+ZnS_3O_6$; and W. Spring, by boiling soln. of the complex thiosulphates: $2HgNaS_2O_3=Hg_2S+Na_2S_3O_6$. The oxidation of a soln. of sodium sulphite and thiosulphate by means of iodine was stated by W. Spring to furnish trithionate by what he supposed to be the reaction: $Na_2SO_3+Na_2S_2O_3+I_2=Na_2S_3O_6+2NaI$, but A. Colefax said that this is not correct, for the trithionate is the result of a secondary reaction between the tetrathionate and sulphite in the presence of the iodine. R. Willstätter obtained the trithionate by dropping hydrogen dioxide into a soln. of sodium thiosulphate at 0° to 10°, $2Na_2S_2O_3+4H_2O_2=Na_2S_3O_6+Na_2SO_4+4H_2O$. F. Raschig said that tetrathionate is produced as an intermediate stage of the reaction; and added that better yields are produced by the reaction $Na_2S_2O_3+2NaHSO_3+2SO_2=H_2O+2Na_2S_3O_6$, in the presence of sodium arsenite—*vide supra*, the pentathionate. J. E. Mackenzie and H. Marshall showed that while tetrathionates are produced by the action of persulphates on thiosulphates—*e.g.* $K_2S_2O_8+2Sr_2S_2O_3-2SrSO_4+K_2S_4O_6$—provided a slight excess of the persulphate is used; if the thiosulphate be in excess, the trithionate is produced. J. von Szilagyi obtained potassium trithionate by the decomposition of potassium arsenothiosulphate: $2K_3As(S_2O_3)_3\rightleftharpoons As_2S_3+3K_2S_3O_6$. P. Pierron found that trithionate is formed in the anodic oxidation of a soln. of ammonium thiosulphate; C. J. Thatcher used sodium thiosulphate—*vide supra*, thiosulphuric acid.

As indicated in connection with Wackenroder's liquid, trithionic acid is found among the products of the decomposition of the polythionic acids; and also by the action of sulphur dioxide on these acids. H. Baumann did not agree with C. Langlois, and F. Kessler, that trithionic acid is formed when dithionates are treated with sulphur. According to W. Spring, when ammonium sulphate is treated with manganese sulphide, in the cold, ammonia and hydrogen sulphide are evolved, and there remain in soln. trithionate and sulphate, but no sulphide; similarly when ammonium sulphate is heated with phosphorus pentasulphide, ammonium trithionate is formed. F. Muck reported that when manganese sulphide is boiled with a soln. of ammonium sulphate, ammonia and hydrogen sulphide are given off, and a small proportion of trithionate is formed. H. Bassett and R. G. Durrant added that the manganese sulphide serves as a source of hydrogen sulphide liberated by the acid derived from the ammonium sulphate. The product is thiosulphate (*q.v.*), not trithionate. They also obtained a little trithionic acid by the action of hydrogen sulphide on sulphuric acid of such a concentration that sulphur is not deposited when a current of hydrogen sulphide is passed through. The sulphuric acid has to be nearly $25N$- before any separation of sulphur occurs on the passage of hydrogen sulphide. It is assumed that the first stage of the action consists in the formation of trithionic acid by reaction with the pyrosulphuric acid present in the conc. acid: $H_2S_2O_7+H_2S\rightleftharpoons H_2S_3O_6+H_2O$. The hydrolysis of the trithionic acid would yield sulphurous and thiosulphuric acid, which, in turn, would give sulphurous acid and sulphur. Sulphur could also be formed by the action of hydrogen sulphide on the intermediate products of hydrolysis. Just as $H_2S_2O_3$ is thionated sulphuric acid, so trithionic acid can be regarded as *thiopyrosulphuric acid.*

M. Hönig and E. Zatzek found trithionate is produced, along with sulphuric acid and sulphur, by the action of potassium permanganate, in the cold, on alkali sulphides or polysulphides. According to W. Spring, sulphur monochloride reacts with potassium sulphite, forming a trithionate: $2K_2SO_3+S_2Cl_2=K_2S_3O_6+2KCl+S$; and sulphur dichloride likewise reacts: $2K_2SO_3+SCl_2=K_2S_3O_6+2KCl$. H. Debus said that water decomposes sulphur monochloride into thiosulphuric and hydrochloric acids and sulphur: $2S_2Cl_2+3H_2O=H_2S_2O_3+4HCl+2S$. The thiosulphuric acid soon splits into water, sulphur, and sulphurous acid. Whenever nascent sulphur and sulphurous acid meet under favourable conditions, polythionic acids are formed, and he detected the presence of pentathionic acid in the liquid—*vide infra.* O. Ruff and E. Giesel observed trithionic acid among the products of the hydrolysis of nitrogen tetrasulphide with water or ammonia.

C. Langlois said that the aq. soln. of the acid is water-clear, and that when highly concentrated, trithionic acid furnishes a syrupy liquid which is not corrosive, is free from smell, and possesses an acidic, astringent, and bitter taste. J. Thomsen gave for the **heat of formation,** $(2SO_2,S,O,Aq.=65{\cdot}886$ Cals.; $(3S,5O,Aq.)=201{\cdot}76$ to 208·03 Cals.; and M. Berthelot, 211·4 Cals.; and M. J. Fordos and A. Gélis observed that the **electrolysis** of the trithionates furnishes potassium hydrosulphate at the anode. H. Hertlein gave 72·8 for the **transport number** of the anion $\frac{1}{2}S_3O_6$ at 25°.

According to W. Petzold, the trithionates are broken down by heat into sulphates, sulphur, and sulphur dioxide; and in aq. soln. the trithionates are hydrolyzed: $2H^{\cdot}+S_3O_6''+H_2O=S_2O_3''+SO_4''+4H^{\cdot}$; but if the soln. is heated, it breaks down: $S_3O_6''=SO_4''+SO_2+S$. There is a state of equilibrium with the pentathionates: $S_5O_6''+S_3O_6''\rightleftharpoons 2S_4O_6''$. The **hydrolysis** of trithionic acid in acidic soln. can be represented by: $H_2S_3O_6+H_2O\rightleftharpoons H_2S+H_2S_2O_7$, and $3H_2S_2O_3+3H_2O\rightleftharpoons 3H_2S+3H_2SO_4$. According to F. Förster and A. Hornig, the hydrolysis in weakly acidic and weakly alkaline soln. can be represented $H_2S_3O_6+H_2O=H_2SO_4+H_2S_2O_3$. The hydrolysis is greatly accelerated by salts of copper, silver, and mercury, with the precipitation of the sulphides of these metals. If the reaction were reversible, the formation of the sulphides could be explained by the decomposition of the thiosulphate, with the consequent disturbance of the equilibrium; but the addition of sulphates does not slow down the rate of hydrolysis, and the presence of barium salts does not accelerate it through the formation of insoluble barium sulphate. H. Bassett and R. G. Durrant suggest that symmetrical and asymmetrical forms of trithionic acid are in equilibrium in the soln.: $HS.SO_2.O.SO_2.OH \rightleftharpoons HO.SO_2.S.SO_2.OH$. The symmetrical form is favoured in alkaline soln., but under ordinary conditions of acidity the asymmetrical form is favoured. The hydrolysis of the asymmetrical form yields hydrogen sulphide and pyrosulphuric acid, and the reaction is greatly accelerated by the salts of copper, silver, and mercury owing to the insolubility of the sulphides; with a barium salt, there is no acceleration because in the equilibria $H_2S_3O_6+H_2O\rightleftharpoons H_2S+H_2S_2O_7$, and $H_2S_2O_7+H_2O\rightleftharpoons 2H_2SO_4$, the pyrosulphuric acid would be hydrated nearly as quickly in the absence of barium as in its presence, since the equilibrium would be almost entirely in favour of sulphuric acid except in very concentrated acid soln. For a similar reason, sulphate ions have little influence on the rate of hydrolysis. A. Kurtenacker and M. Kaufmann, and F. Förster and A. Hornig found that in the absence of salts of the heavy metals, neutral and acidic soln. furnish chiefly sulphate and thiosulphate; and in the presence of sodium acetate, F. Förster found that the reaction: $H_2S_3O_6+H_2O=H_2SO_4+H_2S_2O_3$ is quantitative. In strongly alkaline soln., A. Kurtenacker and M. Kaufmann observed no sulphate, but only sulphite and thiosulphate: $2H_2S_3O_6+3H_2O=H_2S_2O_3+4H_2SO_3$. In the hydrolysis of symmetrical trithionic acid, H. Bassett and R. G. Durrant said that the absence of sulphate indicates that in the first stage of the hydrolysis, the hydroxyl group becomes attached to the central sulphur atom, and not to a terminal one, so as to form a molecule of sulphonic acid, and an unstable intermediate compound, *thiopermonosulphuric acid*, $HO.S.SO_2.OH$, thus:



$$\begin{array}{ll} HO.SO_2 & S.S.O_2.OH \\ \quad H & .OH \end{array} = H.SO_2.OH+HO.S.SO_2.OH$$

The subsequent further hydrolysis of the thiopermonosulphuric acid yields sulphoxylic acid and another molecule of sulphonic acid: $OH.S.SO_2.OH+H_2O \rightarrow S(OH)_2+H.SO_3H$. The sulphoxylic acid is then oxidized to sulphurous acid by another molecule of thiopermonosulphuric acid, which is itself reduced to thiosulphate: $S(OH)_2+OH.S.SO_2.OH \rightarrow H_2SO_3+H_2S_2O_3$. The final result of the hydrolysis in alkaline soln. is represented by the equation: $2H_2S_3O_6+3H_2O \rightleftharpoons H_2S_2O_3+4H_2SO_3$. It was not found possible to synthesize trithionic acid from sulphoxylic and sulphurous acids by boiling a soln. of a mol of formaldehyde-sulphoxylate with $1\frac{1}{2}$ mols of sodium pyrosulphite.

Returning to the hydrolysis $2H_2S_3O_6+3H_2O=H_2S_2O_3+4H_2SO_3$ studied by A. Kurtenacker and M. Kaufmann, with decreasing alkalinity of the soln., sulphate as well as sulphite and thiosulphate is formed; and in the presence of sodium acetate—*i.e.* under nearly neutral conditions—sulphate and thiosulphate were found by F. Förster to be produced on equimolar proportions. The rapid hydrolysis of trithionate in strongly acid soln. yields more than one-third the original sulphur in the form of sulphate. H. Bassett and R. G. Durrant said that sulphate and thiosulphate are never formed by the direct hydrolysis of trithionate—the asymmetrical form of trithionic acid yields hydrogen sulphide and pyrosulphuric acid; and the hydrolysis of the symmetrical form yields, in three stages, as indicated above: $2H_2S_3O_6+3H_2O=H_2S_2O_3+4H_2SO_3$. If both forms of trithionic acid were present in equal proportions, and hydrolyzed at the same time, the asymmetrical acid would yield in two stages: $H_2S_3O_6+2H_2O\rightleftharpoons 2H_2SO_4+H_2S$—F. Kessler observed the formation of hydrogen sulphide during the acid hydrolysis of trithionates—and the symmetrical acid in two stages: $H_2S_3O_6+2H_2O\rightleftharpoons 2H_2SO_3+S(OH)_2$. The hydrogen sulphide from the one would react with the sulphoxylic acid of the other: $H_2S+S(OH)_2\rightleftharpoons 2S+2H_2O$; and the sulphur would react with the sulphurous acid: $H_2SO_3+S=H_2S_2O_3$. This balanced state of the two modes of hydrolysis seems to occur in neutral soln., the resultant reaction being $H_2S_3O_6+H_2O\rightleftharpoons H_2SO_4+H_2S_2O_3$. The formation of polythionic acids in the acid hydrolysis of trithionates is due to later changes. A. Sander represented the reaction with **hydrogen dioxide:** $Na_2S_3O_6+4H_2O_2+4NaOH=3Na_2SO_4+6H_2O$. A. Longi and L. Bonavia found that **sodium dioxide** completely oxidizes trithionates to sulphates. According to M. Berthelot, when **chlorine** is passed into a soln. of a thiosulphate, sulphuric acid or a sulphate is formed; likewise also with **bromine** where the heat of oxidation is 161·6 Cals. J. A. Muller said that action of **iodine** on cold, neutral soln. of trithionates, or soln. acidified with acetic acid is very slow; but is faster with warm soln. C. Langlois said that **hydrochloric acid** has no action on trithionic acid, W. Spring said that hydrochloric acid does not decompose trithionic acid in the cold, but when heated hydrogen sulphide and sulphur are formed. M. J. Fordos and A. Gélis found that trithionates are decomposed by conc. hydrochloric acid without liberating trithionic acid; similarly also with **iodic acid,** and with **chloric acid.** C. Langlois observed that trithionic acid is oxidized by chloric acid, forming sulphur, sulphuric acid, and chlorine, while **perchloric acid** is without action. H. Debus represented the reversible action of **sulphur** on potassium trithionate by: $K_2S_3O_6+S\rightleftharpoons K_2S_4O_6$; and $K_2S_3O_6+2S\rightleftharpoons K_2S_5O_6$. H. Debus observed that while tetrathionic and pentathionic acids are decomposed by **hydrogen sulphide,** trithionic acid, a far less stable compound, which is slowly evolving sulphur dioxide, is not acted upon by that gas at ordinary temp. W. Petzold confirmed this. According to H. Debus, tetrathionic and pentathionic acids react with hydrogen sulphide, forming water and sulphur, but no sulphuric acid. The hydrogen of the hydrogen sulphide reacts with the oxygen of these two polythionic acids. During their spontaneous decomposition in aq. soln., sulphur is separated, but no sulphur is produced; on the other hand, an aq. soln. of trithionic acid is steadily decomposing with the formation of sulphuric acid. Hence, continued H. Debus, the arrangement of the atoms in the trithionate must be such that the affinity of sulphur for oxygen is easily satisfied. When a soln. of trithionic acid is saturated with hydrogen sulphide, there are two influences at work: (i) the affinity of sulphur atoms for oxygen atoms, and (ii) the affinity of the hydrogen of hydrogen sulphide for the oxygen of the trithionate. These opposing influences counterbalance one another so that a soln. of trithionic acid saturated with hydrogen sulphide is more stable than the soln. of trithionic acid alone. If hydrogen sulphide is passed into a mixture of tri-, tetra-, and pentathionic acids, the trithionic acid quickly disappears; tetra- and penta-thionic acids with hydrogen sulphide produce water and sulphur; sulphur *in statu nascendi,* combining with trithionic acid, forms respectively tetrathionic and pentathionic acids—*vide supra,* polythionic acid. Hydrogen sulphide acts on potassium trithionate much more slowly than it does on the penta- or tetra-thionate. A soln. of the trithionate, saturated with hydrogen sulphide, had to stand three days before all the hydrogen sulphide was decomposed. The liquid deposited much sulphur, and the other products of the reaction were $2K_2S_3O_6+5H_2S=K_2SO_4+K_2S_2O_3+5H_2O+8S$—the odour of sulphur dioxide could be also perceived. G. Chancel and E. Diacon, and A. Kurtenacker and M. Kaufmann found that **potassium sulphide** converts the trithionate into thiosulphate without the separation of sulphur: $K_2S_3O_6+K_2S=2K_2S_2O_3$, and W. Spring obtained an analogous result with lead trithionate and sulphide. W. Petzold said that trithionates are stable in the presence of **sulphur dioxide.** The reaction was studied by W. Feld, and F. Oberdick. H. Debus showed that if a soln. of trithionic acid be treated with sulphur dioxide, all three polythionic acids—tri-, tetra-, and penta-—will be in the liquid after some time—*vide supra,* polythionic acids; any **thiosulphuric** acid which is formed reacts with the trithionic acid, forming tetra- and penta-thionic acids. W. Spring said that dil. **sulphuric acid** does not act on trithionic acid in the cold, but when boiled, hydrogen sulphide and sulphur are formed; conc. sulphuric acid was found by C. Langlois to heat the soln. and so decompose the trithionic acid. H. Debus said that dil. sulphuric acid neither accelerates nor retards the decomposition of the trithionates; and M. J. Vordos and A. Gélis said that conc. sulphuric acid develops heat with the separation of sulphur and the evolution of sulphur dioxide.

C. Langlois observed that with **nitric acid,** nitric oxide is given off, sulphur is deposited and transformed into sulphuric acid, and M. J. Fordos and A. Gélis made a similar observation with respect to the trithionates. According to A. Gutmann, sodium trithionate is reduced to the sulphite by **sodium arsenite** dissolved in soda-lye; and the amounts of arsenate and thioarsenate formed agree with the equation: $Na_2S_3O_6+2Na_3AsO_3+2NaOH=2Na_2SO_3+Na_3AsSO_3+Na_3AsO_4+H_2O$. The reaction was discussed by T. S. Price and D. F. Twiss, and J. E. Mackenzie and H. Marshall—*vide supra*, polythionic acids. F. Raschig said that the trithionates react quantitatively with **cyanides** in hot alkaline soln. to form sulphites. This reaction was found by A. Kurtenacker and A. Fritsch to be incomplete in neutral soln., whereas tetrathionates in alkaline soln. give sulphites as well as thiosulphates. E. Weitz and F. Achterberg obtained salts with benzidine.

F. Muck represented the reaction with **sodium**: $K_2S_3O_6+2Na=KNaS_2O_3+KNaSO_3$, and with more sodium, the thiosulphate is converted into sulphide and sulphite. According to M. J. Fordos and A. Gélis, when a trithionate is warmed with an excess of **potassium hydroxide,** sulphite and thiosulphate are formed: $2K_2S_3O_6+6KOH=K_2S_2O_3+4K_2SO_3+3H_2O$, and a trace of sulphate. M. Berthelot added that the reaction does not occur in the cold, and in hot soln. it is attended by the development of much heat. F. Kessler represented the reaction with boiling alkali-lye, $K_2S_3O_6+2KOH=K_2S_2O_3+K_2SO_4+H_2O$, and lead acetate does not give a black precipitate with the soln. A. Kurtenacker and M. Kaufmann said that the decomposition is slow in the case of dil. alkali and probably follows F. Förster and A. Hönig's equation $S_3O_6''+2OH'=S_2O_3''+SO_4''+H_2O$, only a trace of pentathionate is formed. E. H. Riesenfeld and G. W. Feld said that when boiled with an excess of alkali-lye, thiosulphate and sulphite are formed: $2S_3O_6''+6OH'=S_2O_3''+4SO_3''+3H_2O$; C. Langlois said that cold soln. of **copper salts** give no precipitate with trithionates; and W. Spring, that a boiling soln. of trithionic acid is completely decomposed by copper sulphate with the precipitation of copper sulphide; the reaction with potassium trithionate only occurs if none or only a trace of sulphite is present; otherwise, the copper sulphate is reduced and cuprous potassium trithionate is formed. E. H. Riesenfeld and co-workers gave the equation: $S_3O_6''+Cu^{\cdot\cdot}+2H_2O=CuS+2SO_4''+4H^{\cdot}$, and added that tetrathionates are indifferent towards this reagent. For the action of aq. and ammoniacal **silver nitrate** soln., *vide* Table XVII. C. Langlois said that with silver nitrates the trithionates give a yellowish-white precipitate which rapidly blackens owing to the formation of silver sulphide. C. Langlois observed no precipitation occurs in the cold with soln. of **calcium, strontium, or barium salts**; likewise also with **salts of magnesium, and zinc.** In the case of the barium salt, barium sulphate may be precipitated when the mixture is heated. According to W. Spring, trithionic acid with a small proportion of **mercurous nitrate** gives a black precipitate which soon turns white—Table XVII; and C. Langlois said that a black precipitate of mercuric sulphide is produced by mercurous salts and trithionates, and with **mercuric salts** the black sulphide passes into white sulphate. W. Spring, and H. Debus observed that with mercuric chloride, a white sulphochloride is precipitated and no free sulphur is formed; and with mercuric cyanide, there is first a yellow precipitate which blackens slowly in the cold, and rapidly when heated. R. Willstätter said that the precipitate with mercuric nitrate is yellowish-brown, and that it blackens when warmed, and whitens when boiled. W. Feld represented the reaction with mercuric chloride: $Na_2S_3O_6+2HgCl_2+2H_2O=Na_2SO_4+2HgCl+H_2SO_4+2HCl+S$; but A. Sander showed that a sulphochloride, $Hg_3S_2Cl_2$, is formed, $2K_2S_3O_6+3HgCl_2+4H_2O=Hg_3S_2Cl_2+4KCl+4H_2SO_4$. C. Langlois said that no precipitation occurs in the cold with **salts of aluminium, lead, uranium, cobalt, and nickel**; while **manganic sulphate** is decolorized. A. Gutmann found that sodium trithionate is reduced by **sodium stannite** and hydroxide to sodium sulphite, stannate, and thiostannate. A. Longi and L. Bonavia said that **potassium permanganate** in alkaline soln. slowly oxidizes trithionate to sulphates. F. Raschig said that in an acidic soln. potassium permanganate oxidizes two-thirds of the trithionate sulphur to sulphate, and the remainder to dithionate. W. Wardlaw and N. D. Sylvester found that acidified soln. of tervalent **molybdenum salts** react with sodium trithionate, forming a brown precipitate as in the case of sodium tetrathionate, possibly with the intermediate formation of *molybdenum trithionate.*

Trithionic acid is dibasic, forming salts called **trithionates,** $M_2'S_3O_6$. Most of these salts are readily soluble in water. The potassium salt is the best known. F. Muck was unable to prepare **ammonium trithionate,** $(NH_4)_2S_3O_6$, by the action of manganese sulphide on ammonium sulphate; ammonia and hydrogen sulphide are given off, but no ammonium sulphide is formed; the soln. probably contains a complex manganese ammonium trithionate. W. Spring heated a mixture of phosphorus pentasulphide and ammonium sulphate, and found that ammonium thiosulphate and polysulphide are given off, while impure ammonium sulphide remains in the residue, and is thought to be formed by the decomposition of the thiosulphate: $2(NH_4)_2S_2O_3=(NH_4)_2S_3O_6+(NH_4)_2S$. This is an unsatisfactory method of preparation. E. Divers and M. Ogawa said that the ammonium salt is so very soluble that it cannot be obtained by the process employed by E. Mathieu-Plessy, and H. Hertlein for the potassium salt; but they obtained it by treating a soln. of the potassium salt with hydrofluosilicic acid, neutralized the clear liquid quickly with ammonia, precipitated the ammonium trithionate with absolute alcohol, and dried it in a desiccator. The very deliquescent, and changeable salt cannot be kept long in good condition. It is scarcely affected by heat until the temp. exceeds 150°, and then it steadily decomposes between 160° and 170°, forming sulphur dioxide, a residue of ammonium sulphate and of unfused sulphur. The non-fusion of the sulphur in attributed to the presence of minute quantities of impurities; it is freely soluble in carbon disulphide and crystallizes out on evaporating the solvent. J. A. Christiansen obtained *p*-toluoyl trithionate.

The methods of preparing potassium trithionate do not succeed so well when employed for **sodium trithionate,** $Na_2S_3O_6.3H_2O$. F. Kessler obtained it by mixing soln. of potassium trithionate and sodium hydrotartrate in the smallest possible quantity of water, cooling rapidly to 0°, and evaporating the clear liquid in vacuo. B. Rathke said that sulphur dioxide is given off, and that sodium sulphate crystals are followed by those of sodium thiosulphate, but not trithionate. C. J. Thatcher obtained it by the electrolysis of a feebly acidic or alkaline soln. of sodium thiosulphate, and by the hydrolysis of an alkaline soln. of tetrathionate. A. Colefax —*vide supra*—observed its formation as a secondary product in the reaction between iodine and a mixture of sulphite and thiosulphate. W. Spring prepared it from sodium mercuric thiosulphate as indicated above; A. Villiers, by the action of sulphur dioxide on sodium thiosulphate; and R. Willstätter, by the action of hydrogen dioxide on sodium thiosulphate. According to A. Villiers, the rhombic prismatic crystals have the axial ratios $a:b:c=0{\cdot}5040:1:0{\cdot}6972$. M. Berthelot gave for the heat of formation $(3S,3O_2,2Na)=393{\cdot}6$ Cals.; and for the heat of soln., $-10{\cdot}14$ Cals. at 10·2°.

As previously indicated, **potassium trithionate,** $K_2S_3O_6$, was prepared by C. Langlois, B. Rathke, W. Spring, E. Mathieu-Plessy, G. Chancel and E. Diacon, H. Hertlein, etc. J. E. Mackenzie and H. Marshall mixed 20 grms. of potassium persulphate, 46 grms. of strontium thiosulphate, and 70 c.c. of water. The filtered liquid was allowed to evaporate spontaneously in a current of air, and filtered each day to remove the deposited sulphur. The tetrathionate was nearly all decomposed by the time the crystals of trithionate began to form. The crystals were dissolved in the minimum quantity of water at about 30°, and the filtered soln. allowed to cool slowly. This treatment was repeated until no sulphur was deposited when the soln. was allowed to stand for 2 or 3 hrs. The soln. saturated at 30° was then allowed to cool slowly for 4–5 days when well-developed crystals were formed. The rhombic, prismatic crystals were found by F. de la Provostaye to have the axial ratios $a:b:c=0{\cdot}7166:1:0{\cdot}4215$. They were also examined by C. F. Rammelsberg, H. E. Merwin, and H. Baker. B. Rathke said that the crystals are monoclinic, but he gave no measurements. J. E. Mackenzie and H. Marshall gave for the axial ratios of the rhombic bipyramids $a:b:c=0{\cdot}7168:1:0{\cdot}4193$. No distinct cleavage was observed; in convergent, polarized light, viewed through the (210)-face, the interference figures showed that the plane of the optic axis is parallel to the (010)-face, with the c-axis as acute bisectrix. The optic axial angle $2V=68°\ 15'$. H. E. Merwin found $2V=72°$ (Na-light); and J. E. Mackenzie and H. Marshall found that the sp. gr. varied from 2·3335 to 2·3395—average, 2·336. H. Hertlein gave for the sp. gr. 2·3036 to 2·3044, and for the mol. vol., 117·39. H. Hertlein found the sp. gr. of soln. with 1·326, 3·281, 6·396, and 11·989 per cent. of the salt to be respectively 1·00868, 1·02148, 1·04234, and 1·08124; and the mol. vol., 94·942, 97·132, 98·683, and 101·00 respectively. C. Langlois found that when heated to redness potassium trithionate decomposes into sulphur, sulphur dioxide, and potassium sulphate: $K_2S_3O_6=SO_2+K_2SO_4+S$. J. Thomsen gave for the heat of formation $(2K,3S,3O_2)=406{\cdot}8$ Cals., and M. Berthelot, 416 Cals. J. Thomsen gave $-13{\cdot}15$ Cals. for the heat of soln.; F. Martin and L. Metz, 401 Cals.; M. Berthelot gave $K_2S_3O_6$aq.$+4Br_2$(soln. in KI)$+6H_2O=3KBr+3H_2SO_4+6HBr+74{\cdot}7$ Cals. at 10°; and for the heat of the reaction with potassium hydroxide, $2K_2S_3O_6$aq.$+6KOH$aq.$=K_2S_2O_3$aq.$+4K_2SO_2$aq.$+3H_2O_3+18{\cdot}5$ Cals. J. E. Mackenzie and H. Marshall found the indices of refraction for Na-light to be $\alpha=1{\cdot}4925$, $\beta=1{\cdot}5646$, and $\gamma=1{\cdot}6014$; and H. E. Merwin gave for light of wave-length λ,:

λ .	436	486	546	578	584	656	691$\mu\mu$
α .	1·5040	1·4993	1·4954	1·4941	1·4934	1·4909	1·4903
β .	1·5805	1·5732	1·5673	1·5649	1·5641	1·5607	1·5591
γ .	1·621	1·612	—	—	1·602	—	1·596

H. Hertlein gave for the sp. refraction of the aq. soln. for Na-light, 0·2392 with the μ-formula, and 0·1401 with the μ^2-formula; the corresponding mol. refractions are 64·69 and 38·15 respectively. V. J. Sihvonen found maxima in the ultra-red reflection spectrum at 8·3μ, 10·0μ, 15·1μ, 16·5μ, and 19·3μ. R. Robl observed no fluorescence when the salt is exposed to ultra-violet light. H. Hertlein gave for the electrical conductivity, μ, at 25° of soln. with a mol of the salt in v litres:

v .	32	64	128	256	512	1024
μ .	114·4	121·0	129·0	133·7	137·9	140·8

According to C. Langlois, and F. Kessler, the salt has a bitter taste; it is stable in air; and has a neutral reaction. It is readily soluble in water, and the soln. decomposes the more rapidly the higher the temp. H. Debus said that when the soln. is allowed to stand for a long time, it forms sulphate, sulphurous acid, and sulphur, and the latter, *in statu nascendi*, unites with the undecomposed trithionate, forming tetrathionate and pentathionate.

J. E. Mackenzie and H. Marshall prepared **rubidium trithionate,** $Rb_2S_3O_6$, as in the case of the potassium salt, but using 20 grms. of rubidium persulphate, 33 grms. of strontium thiosulphate, and 40–50 c.c. of water. Rubidium trithionate is more soluble than the potassium salt. The crystal of the two salts are isomorphous. The long prismatic crystals are rhombic bipyramids with the axial ratios $a:b:c=0{\cdot}7058:1:0{\cdot}4176$, with the optic axial angle $2V=62°\ 33'$. The optical characters are similar. The sp. gr. is 2·843 to 2·847—average 2·845—and the mol. vol. 127·7. The indices of refraction are $\alpha=1{\cdot}4874$, $\beta=1{\cdot}5580$, and $\gamma=1{\cdot}5867$. **Cæsium trithionate,** $Cs_2S_3O_6.H_2O$, was obtained from 32 grms. of cæsium persulphate, 45 grms. of strontium thiosulphate, and 60 c.c. of water. The crystals belong to the triclinic system, but they could not be measured satisfactorily owing to their rapid efflorescence. The sp. gr. is 3·189 to 3·196—average 3·192—and the mol. vol. 149·1. By slowly cooling a hot alcoholic soln. from 50°, the anhydrous salt was obtained. The crystals were not well-developed. The sp. gr. is 3·326.

C. Langlois found that **copper trithionate** is soluble in water and very unstable —*vide supra*—decomposing in soln. with the precipitation of copper sulphide. G. T. Morgan and F. H. Burstall found that the salt can be stabilized by union with ethylenediamine; and they prepared **copper bisethylenediaminotrithionate,** $[\mathrm{Cu\ en_2}]\mathrm{S_3O_6}$, by adding an aq. soln. of 7·1 grms. of sodium trithionate to a cold soln. of 5·9 grms. of copper acetate, and 3·6 grms. of ethylenediamine; and then adding an excess of alcohol to the purple, filtered soln. The salt was recrystallized from lukewarm water, and dried in a desiccator. Copper bisethylenediaminotrithionate is quite stable in the air under normal conditions, but on heating it decomposes without melting at 170°–175°. Silver nitrate gives, in the cold, a white precipitate, rapidly becoming yellow and finally black; this decomposition is greatly facilitated by warming. Barium chloride has no action in the cold, but on heating a white precipitate is formed. Sodium hydroxide causes the purple aq. soln. to become blue, whereas dil. acids discharge the intense colour, with deposition of copper sulphide. C. Langlois observed that while trithionic acid does not give a precipitate with ammoniacal silver nitrate, a soln. of a trithionate, when treated with silver nitrate, gives a yellowish-white precipitate of **silver trithionate** which rapidly decomposes into silver sulphate and sulphide. **Calcium trithionate,** and **strontium trithionate** have been obtained only in aq. soln. C. Langlois prepared **barium trithionate,** $\mathrm{BaS_3O_6.2H_2O}$, by the action of baryta-water on trithonic acid; F. Kessler, by saturating trithionic acid with barium carbonate, and precipitating with alcohol; and W. Spring, by the action of sulphur monochloride on barium sulphite. The tabular crystals are soluble in water, and the soln. quickly decomposes with the separation of barium sulphate. **Magnesium trithionate** has been obtained only in aq. soln. M. J. Fordos and A. Gélis obtained **zinc trithionate** among the products remaining on evaporating a soln. of zinc thiosulphate. The soln. of zinc trithionate readily decomposes on evaporation into sulphur, sulphur dioxide, zinc sulphide, and sulphate. W. E. Henderson and H. B. Weiser said that the soln. decomposes when evaporated in vacuo at 40°. **Mercurous trithionate** and **mercuric trithionate** are sparingly soluble but rapidly decompose—*vide supra.* F. Kessler represented the action of heat on mercuric trithionate: $\mathrm{HgS_3O_6} = \mathrm{HgS} + 2\mathrm{SO_3}$; **aluminium trithionate** has been obtained only in aq. soln. E. J. Bevan prepared **thallium trithionate,** $\mathrm{Tl_2S_3O_6}$, by evaporating a soln. of thallous carbonate in trithionic acid. The colourless, acicular crystals are isomorphous with those of the potassium salt. They decompose slowly at ordinary temp., rapidly when heated; and on this account it is difficult to prepare the salt free from sulphate. C. Langlois obtained **lead trithionate,** $\mathrm{PbS_3O_6}$, from an aq. soln. of trithionic acid and a lead salt. F. Kessler also prepared this salt. When dried in vacuo, J. Fogh said that the salt is anhydrous, and he obtained it by allowing a mixture of sat. soln. of lead acetate and sodium trithionate to stand for several days in a closed flask. He also said that it is formed when lead thiosulphate is boiled with water, $2\mathrm{PbS_2O_3} = \mathrm{PbS} + \mathrm{PbS_3O_6}$, but W. H. Perkins and A. T. King said that there is no justification for this statement. C. Langlois obtained lead trithionate as a white precipitate which becomes black when heated. J. Fogh said that the acicular crystals are stable at ordinary temp., but when heated give off sulphur dioxide. The heat of formation is 285·2 Cals.; and the heat of soln., —5 Cals. G. Chancel and E. Diacon found that the salt is sparingly soluble in water; it is also soluble in a soln. of sodium thiosulphate, and, added A. and L. Lumière and A. Seyewetz, this soln. is very unstable. **Uranium trithionate** has been obtained only in aq. soln., and a similar remark applies to **cobalt trithionate,** and **nickel trithionate.** L. Vanino and F. Mussgnug were unable to prepare normal **bismuth trithionate,** $\mathrm{Bi_2(S_3O_6)_3}$, by the action of sodium trithionate on a bismuth-mannitol soln.

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§ 43. Tetrathionic Acid and the Tetrathionates

In 1842, M. J. Fordos and A. Gélis,[1] in their memoir *Sur un nouvel oxacide du soufre*, said that the hyposulphites (thiosulphates) were *en quelque sorte oubliés des chimistes* until M. Daguerre employed sodium thiosulphate in his work on photography. This stimulated interest in this salt. They tried to analyze the salt by treating its aq. soln. with chlorine so as to transform the sulphur into sulphuric acid, but the deposit of sulphur which was obtained was very difficult to separate by filtration. They then tried iodine, expecting that, as in the case of sulphites, the sulphur would be oxidized to sulphuric acid and the iodine reduced to hydriodic acid ; but the result was different. With iodine and a soln. of barium thiosulphate, no barium sulphate was precipitated and a clear soln. was obtained. They therefore investigated *cette réaction curieuse*. A soln. of sodium thiosulphate was treated with iodine ; much iodine was absorbed, without producing any deposit or changing the colour of the liquid. When the soln. was saturated with iodine, any further addition produced a yellow coloration. The liquid then contained no sulphate, sulphuric acid, or any substance capable of giving a precipitate with a barium salt. The water was not decomposed, and no acid was formed, for the liquid was neutral before and after the operation ; it was without odour, and this would not have been the case if it contained sulphurous acid. Commercial sodium thiosulphate absorbs about half its weight of iodine. The crystals contain 5 eq. of water, so that 1 grm. of the salt contains 0·638 grm. of anhydrous thiosulphate ; and 1 mol of the salt absorbs a gram-atom of iodine. The iodine is present in the soln. as iodide, for the liquid gives all the reactions characteristic of the iodides. Since no sulphuric or sulphurous acid is formed during the action of iodine on the thiosulphate, and no precipitation of sulphur occurs, it is natural to assume that the iodine removes from the thiosulphate half its combined sodium and the residues combine together in pairs, forming the sodium salt of a new acid, $H_2S_4O_6$, analogous to C. Langlois' *l'acide sulfhyposulfurique*, $H_2S_3O_3$, but richer in sulphur. The reaction is represented by the equation $2Na_2S_2O_3+I_2=2NaI+Na_2S_4O_6$.

M. J. Fordos and A. Gélis precipitated a conc. soln. of sodium thiosulphate with barium acetate, and washed the product with dil. alcohol ; they stirred up the product with water, and added iodine in small quantities at a time so as to form a soln. of barium iodide and tetrathionate. Barium iodide was washed from the crystallized product by means of alcohol. The resulting barium tetrathionate was treated with sulphuric acid (1 : 4) in the cold. The filtered liquid was evaporated in vacuo over sulphuric acid. F. Kessler added that the soln. of the acid so obtained is not quite pure since in the presence of strong bases, it is resolved into trithionic acid and sulphur. He treated lead thiosulphate with iodine, and filtered off the lead iodide ; he then precipitated the lead from the lead tetrathionate soln. by sulphuric acid ; and finally removed the sulphuric acid by barium carbonate. The filtered liquid was then evaporated on a water-bath. The lead cannot be precipitated by hydrogen sulphide because tetrathionic acid is decomposed by that gas. H. Debus obtained soln. of the acid by treating the potassium salt with the calculated quantity of tartaric acid, and, after two days, filtering the liquid.

Tetrathionic acid exists only in aq. soln. ; neither **tetrathionic acid,** $H_2S_4O_6$, nor **tetrathionic anhydride,** S_4O_5, has been prepared. The aq. soln. has about the same stability as dithionic acid. M. J. Fordos and A. Gélis said that the dil. aq. soln. can be boiled without decomposition, but the conc. soln. decomposes into sulphur, sulphur dioxide, and sulphuric acid. F. Kessler said that the acid is not decomposed by boiling, and added that M. J. Fordos and A. Gélis's product probably contained sulphuric acid. H. Hertlein said that tetrathionic acid is *ziemlich unbeständig*. H. Debus showed that an aq. soln. of potassium tetrathionate at 18° slowly decomposes into the pentathionate and trithionate, sulphurous acid, and potassium sulphate. The first action is symbolized : $2K_2S_4O_6=K_2S_5O_6+K_2S_3O_6$, and, as previously indicated, the trithionate decomposes : $3K_2S_3O_6=2K_2SO_4+2SO_2+K_2S_5O_6$. The crystals of the potassium salt smelt of sulphur dioxide after being kept in a closed bottle for some time ; the decomposition is produced by water enclosed in cracks and fissures in the crystals ; the thoroughly dried salt can be kept without the slightest change. A. Kurtenacker and M. Kaufmann said that, as indicated by H. Debus, potassium tetrathionate, in soln., forms a mixture of thionates, resembling that with the pentathionates. They get the necessary sulphur when the tetrathionate forms trithionate : $S_4O_6''=S_3O_6''+S$. H. Hertlein said that potassium tetrathionate is relatively stable in aq. soln. ; while the barium salt is unstable. T. Curtius found that an aq. soln. of barium tetrathionate decomposes into barium thiosulphate, thiosulphuric acid, and oxygen, and these compounds subsequently decompose into sulphur, sulphur dioxide, and sulphate ; and if the soln. of barium tetrathionate is treated with alcohol the thiosulphate is formed —G. A. Lenoir regarded the precipitate as barium pentathionate. G. Chancel and E. Diacon added that copper tetrathionate decomposes slowly at ordinary temp., forming the sulphide ; the change is rapid at a higher temp.

The iodine process was used by A. Schwicker, N. von Klobukoff, H. Hertlein, F. Kessler, etc. A. Sander showed that the presence of thiosulphate accelerates the decomposition of the tetrathionate, not, as suggested by W. Feld, by the reaction

$Na_2S_4O_6+2Na_2S_2O_3=5S+3Na_2SO_4$, but rather by a purely catalytic effect. Potassium tetrathionate of a high degree of purity can be obtained as follows:

> To a cooled soln. of 26 grms. of iodine in alcohol is added, drop by drop, a sat. soln. in water of 50 grms. of sodium thiosulphate or 39·5 grms. of potassium thiosulphate. The tetrathionate, which separates out as it is formed, is collected, and washed with alcohol until it is free from iodine and iodide, dissolved in a little water, and again precipitated by alcohol. After drying over sulphuric acid, it can be kept for many months without undergoing decomposition.

As indicated in connection with thiosulphates, the cyanogen halides form some tetrathionate. As indicated in connection with the thiosulphates, other oxidizing agents produce some tetrathionate; thus, M. J. Fordos and A. Gélis, and F. Diénert and F. Wandenbulcke, and G. Lunge observed that this occurs with hypochlorites—*vide supra*, the thiosulphates, and trithionates; M. J. Fordos and A. Gélis, with chlorates; E. Sonstadt, with iodates: $6Na_2S_2O_3+KIO_3+6HCl=3Na_2S_4O_6+KI+6NaCl+3H_2O$; A. Benrath and K. Ruland, ceric sulphate; M. J. Fordos and A. Gélis, ferric salts: $2Na_2S_2O_3+2FeCl_3=2NaCl+2FeCl_2+Na_2S_4O_6$—J. Scherer added that in warm or in acidic soln. some sulphate is formed; G. Chancel and E. Diacon, barium or lead dioxide: $2PbS_2O_3+PbO_2+2H_2SO_4=PbS_4O_6+2PbSO_4+2H_2O$, and A. Nabl, hydrogen dioxide: $2Na_2S_2O_3+H_2O_2=Na_2S_4O_6+2NaOH$, provided that the sodium hydroxide is neutralized as it is formed, otherwise the alkali hydroxide decomposes the tetrathionate into thiosulphate, sulphate, and sulphite. R. Willstätter studied this reaction—*vide supra;* M. J. Fordos and A. Gélis, and G. Chancel and E. Diacon observed that the reduction of cupric to cuprous salts is accompanied by the oxidation of thiosulphate to tetrathionate. C. F. Rammelsberg observed that this occurs with potassium thiosulphate, and E. Zettnoff, with sodium thiosulphate. J. J. van Renesse represented the reaction: $2CuSO_4+3Na_2S_2O_3=Cu_2S_2O_3+Na_2S_4O_6+2Na_2SO_4$. G. Vortmann stated that sulphuric acid is not produced, although M. Siewert, and F. Kessel reported that it is formed. G. Vortmann observed the formation of the complex salt which C. and I. Bhaduri said decomposes: $3Cu_2S_2O_3.2Na_2S_2O_3.8H_2O=3Cu_2S+2Na_2SO_4+H_2SO_4+2S+2SO_2+7H_2O$. H. Bassett and R. G. Durrant said that the formation of the complex salt and tetrathionate agrees with $2CuCl_2+4Na_2S_2O_3+H_2O=Na_2S_2O_3.Cu_2S_2O_3.H_2O+Na_2S_4O_6+4NaCl$, in which no sulphuric acid is formed. Any sulphuric acid found by M. Sievert, and F. Kessel is attributed to the partial decomposition of one of the complex salts; and J. J. van Renesse indicated that cuprous thiosulphate is produced, but if so, it must be very unstable. F. Raschig obtained potassium tetrathionate by oxidizing the thiosulphate with copper sulphate: $3Na_2S_2O_3+2CuSO_4=Cu_2S_2O_3+2Na_2SO_4+Na_2S_4O_6$, and then treating the product with potassium acetate. The potassium tetrathionate is then washed with alcohol. H. Marshall observed that thiosulphates are oxidized to tetrathionates by persulphates: $2SrS_2O_3+K_2S_2O_8=2SrSO_4+K_2S_4O_6$—owing to the sparing solubility of barium thiosulphate, J. E. Mackenzie and H. Marshall found it better to use the more soluble strontium salt; J. F. Norris and H. Fay, selenium dioxide, $4Na_2S_2O_3+SeO_2=2Na_2S_4O_6+Se+2Na_2O$; H. Bassett and R. G. Durrant, methylene-blue in strongly acid soln.; and H. Debus, W. Feld, F. Raschig, and A. Villiers, the passage of sulphur dioxide, when tri- and penta-thionates are also formed. G. Vortmann observed that tetrathionate is formed when arsenic trioxide, antimony trichloride, or stannous or stannic chloride is allowed to act on sodium thiosulphate: $As_2O_3+9Na_2S_2O_3=As_2S_5+3Na_2S_4O_6+3SO_2+6Na_2O$. W. Spring likewise said that tetrathionate is formed when sulphur dichloride or sulphur monochloride acts on potassium thiosulphate; and H. Debus, by the action of sulphur dioxide and water on sulphur monochloride—there are formed at the same time hydrochloric, sulphuric, and pentathionic acids, and sulphur. W. Spring added that trithionate not tetrathionate is formed by the action of sulphur monochloride on potassium sulphite. P. Pierron obtained tetrathionate as a product of the anodic oxidation of sodium thiosulphate; F. J. Faktor also obtained it in the electrolysis of sodium thiosulphate; and C. J. Thatcher, by the electrolysis of neutral soln. with between —0·75 and —0·95 volt.

The formation of tetrathionic acid in the action of hydrogen sulphide on sulphurous acid has been discussed in connection with the polythionates, and Wackenroder's liquid (*q.v.*). W. Spring represented the reaction $SO_2+2H_2S=2H_2O+3S$; $SO_2+H_2O+S=H_2S_2O_3$; $SO_2+2H_2S_2O_3=H_2SO_2+H_2S_4O_6$. He said that tetrathionic acid can be formed by the action of sulphur dioxide on flowers of sulphur; he thought that the indigo-blue colour which may appear indicates the formation of hyposulphurous acid which he symbolized H_2SO_2. The blue colour, of course, may indicate colloidal sulphur. H. Debus added that only when *in statu nascendi* will sulphur react with sulphur dioxide. T. Curtius and F. Henkel agitated Wackenroder's liquid with an excess of barium carbonate, and dropped the liquid, before it began to decompose, into absolute alcohol—each drop gave a crystalline precipitate of barium tetrathionate which could be dissolved in a little water, and again precipitated by alcohol. V. Lewes added enough baryta-water to Wackenroder's liquid to neutralize about one-half; and next day filtered off the sulphur, and the barium sulphate. When evaporated in vacuo, sulphur separates out, and in about three weeks, barium tetrathionate appears. The mother-liquor furnishes the pentathionate. The tetrathionate so prepared is identical with that obtained from the thiosulphate and iodine. T. Curtius said that barium carbonate decomposes the pentathionic acid in Wackenroder's liquid into the tetrathionate: $H_2S_5O_6+BaCO_3=BaS_4O_6+CO_2+H_2O+S$. According to W. Spring, the addition of alcohol to a soln. of barium tetrathionate yields a precipitate not wholly soluble in water. This insoluble portion is stated by T. Curtius to be barium thiosulphate. The salts prepared by V. Lewes's process are said to be of variable composition, and T. Curtius obtained well-formed salts, by evaporating down the half-neutralized soln., with carbonates of the weak bases, such as zinc, and filtering off the sulphur and excess of carbonate. By this means, an acid liquid is produced, which, when heated in small quantities in a test-tube, explodes, yielding sulphur, zinc sulphide, sulphurous acid, and hydrogen sulphide; if, however, the soln. is slowly evaporated at a low temp., the whole solidifies on cooling to a crystalline mass consisting of non-deliquescent crystals. The zinc salt is soluble in water; the didymium compound forms hard, sandy, transparent, rose-coloured crystals, of acid reaction, soluble in water, but precipitated from soln. as a red powder by alcohol. The manganese salt is pale red, soluble in water, and deliquescent. All the salts can be preserved unaltered, but at 100° sulphur is separated, as also are sulphurous acid and hydrogen sulphide. V. Lewes's compounds, when decomposed, do not produce hydrogen sulphide, and therefore they cannot be identical with those obtained by T. Curtius. W. Spring said that tetrathionic acid is formed in the reaction between sulphur dioxide and hydrogen disulphide and at the same time sulphur and hyposulphurous acid are formed. According to G. Chancel and E. Diacon, tetrathionic acid is formed when lead dioxide is warmed with pentathionic acid: $4H_2S_5O_6+5PbO_2=5PbS_4O_6+4H_2O$; and it is formed in the spontaneous decomposition of pentathionic acid.

The aq. soln. of tetrathionic acid is colourless and without taste or smell. J. Thomsen gave for the heat of formation $(4S,6O,H_2Aq.)=273·32$ Cals.; $(4S,5O,Aq.)=204·96$ Cals.; $(2SO_2,O,2S,Aq.)=62·82$ Cals.; $(2SO_2,O,S_2,Aq.)=47·42$ Cals.; $(2S_2O_2Aq.,O)=53·489$ Cals.; and M. Berthelot gave $(4S,5O,H_2OAq.)=205·2$ Cals. J. Thomsen gave 27·07 Cals. for the heat of neutralization. W. Ostwald found the mol. conductivity for soln. with a mol of the acid in v litres of water at 25°:

v	16	64	256	1024	4096	8192
μ	165·4	174·0	181·5	186·1	188·6	187·2

The result is said to be above the maximum characteristic of dibasic acids—probably owing to decomposition. H. Hertlein gave for the eq. conductivity in mercury units at 25°:

v	43·18	86·36	172·72	345·44	690·88	1381·76
λ	361·6	371·3	380·2	390·0	400·0	406·6

The acid had not a very high degree of purity, the ionization is 92 per cent., so that the acid is stronger than dithionic acid. I. M. Kolthoff said that tetrathionic acid is one of the strongest of the dibasic acids. M. Rudolphi calculated values for the degree of ionization on the assumption that the acid is monobasic. K. Jellinek found that the failure of the mass law prevented him calculating the ionization constants of this acid. H. Hertlein found that the transport number for the anion $\frac{1}{2}S_4O_6$ is 67·4 at 25°.

F. Calzolari said that tetrathionic acid, $HO.SO_2.S.S.SO_2.OH$, and persulphuric acid, $HO.SO_2.O.O.SO_2.OH$, possess a similar structure, and exhibit various analogies —*e.g.* the tetrathionates furnish compounds with ammonia, pyridine, and hexamethylenetetramine which are similar in external form, composition, and solubility with those furnished by the persulphates. T. S. Price and D. F. Twiss also emphasized the relationship between the persulphates and tetrathionates. W. Petzold found that the tetrathionates are the most stable of the polythionates when heated, and in aq. soln., the tetrathionates slowly decompose into trithionate and sulphur; and there is a state of equilibrium between the trithionates and pentathionates: $S_5O_6'' + S_3O_6'' \rightleftharpoons 2S_4O_6''$, corresponding with the greater stability of the tetrathionates. C. J. Thatcher observed that the tetrathionates are reduced by **hydrogen** in neutral or alkaline soln., with or without the presence of platinum, forming thiosulphate.

F. Förster and A. Hornig, and A. Kurtenacker and M. Kaufmann studied the **hydrolysis** of trithionic acid (*q.v.*), and of tetrathionic and pentathionic acids. According to H. Bassett and R. G. Durrant, trithionic acid is always formed when tetrathionic and pentathionic acids are hydrolyzed. This occurs by direct decomposition: $H_2S_5O_6 \rightleftharpoons H_2S_4O_6 + S$, and $H_2S_4O_6 \rightleftharpoons H_2S_3O_6 + S$, and possibly $H_2S_5O_6 \rightleftharpoons H_2S_3O_6 + S_2$, or else by the intervention of sulphurous and thiosulphuric acids, which are products of the hydrolyses of trithionic acid: $H_2S_4O_6 + H_2SO_3 \rightleftharpoons H_2S_3O_6 + H_2S_2O_3$; $H_2S_5O_6 + H_2SO_3 \rightleftharpoons H_2S_4O_6 + H_2S_2O_3$; and $H_2SO_3 + S \rightleftharpoons H_2S_2O_3$. It is probable that the decompositions of tetrathionic and pentathionic acids are bimolecular so that the reactions are symbolized: $2H_2S_5O_6 \rightleftharpoons 2H_2S_4O_6 + S_2$, and $2H_2S_4O_6 \rightleftharpoons 2H_2S_3O_6 + S_2$. The final products of the hydrolysis of trithionic, tetrathionic, and pentathionic acids are sulphuric acid, sulphur dioxide, and sulphur with a small quantity of hydrogen sulphide in the intermediate stages as noted by F. Kessler. The hydrolyses in alkaline soln. are symbolized by A. Kurtenacker and M. Kaufmann: $2H_2S_3O_6 + 3H_2O \rightleftharpoons H_2S_2O_3 + 4H_2SO_3$; $2H_2S_4O_6 + 3H_2O \rightleftharpoons 3H_2S_2O_3 + 2H_2SO_3$; and $2H_2S_5O_6 + 3H_2O \rightleftharpoons 5H_2S_2O_3$. In the case of tetra- and penta-thionates, the tri- and tetra-thionates are formed to some extent as intermediate steps, and in absence of sufficient hydroxyl-ion conc. some hydrolysis of trithionate in the manner characteristic of acid conditions occurs, with consequent formation of sulphate. The equations just indicated are only summation equations. The hydrolysis of tetrathionic and pentathionic acids can be explained in a similar way to that of trithionic acid (*q.v.*). The fact, observed by F. Raschig, that when pentathionate is treated with sodium carbonate it loses one atom of sulphur to form tetrathionate, not two atoms to form trithionate, suggests that in alkaline soln. the tetrathionate has the straight-chain structure, although it would seem to pass readily into the other form, $OH.SO_2.S(S).SO_2.OH$, since sulphite converts it into trithionate. Hydrolysis of the straight-chain form would yield one mol. of thiosulphate and one mol. of thiopermonosulphuric acid, which would then give rise to thiosulphate and sulphite, as already indicated. Complete alkaline hydrolysis of tetrathionate would thus take place in accordance with the equation: $2H_2S_4O_6 + 3H_2O = 3H_2S_2O_3 + 2H_2SO_3$. The sulphur dropped by pentathionic acid: $H_2S_5O_6$ $H_2S_4O_6 + S$ in forming tetrathionic acid suffices to convert a mol. of sulphite into thiosulphate, so that in this case complete alkaline hydrolysis yields nothing but thiosulphate: $2H_2S_5O_6 + 3H_2O \rightleftharpoons 5H_2S_2O_3$. In the acid hydrolysis of pentathionic acid, if the hydroxyl group becomes attached to the central sulphur atom, as in the case of trithionic acid, the first step would furnish dithiodithionic acid:

$HO.SO_2.S(:S_2).SO_2.OH+H_2O=H.SO_2.OH+HO.S(:S_2).SO_2.OH$ (dithiodithionic acid); this would be unstable and might break up into sulphur and thiopermonosulphuric acid which would then react as indicated in connection with trithionic acid. It is possible that $HO.S(.S).SO_2.OH$ is formed as an intermediate compound by the acid hydrolysis of the asymmetrical form of tetrathionic acid, $HO.SO_2.S(.S).SO_2.OH$.

A. Sander represented the reaction with **hydrogen dioxide:** $Na_2S_4O_6+7H_2O_2+6NaOH=4Na_2SO_4+10H_2O$; and A. Longi and L. Bonavia found that the tetrathionates are immediately and completely oxidized by **sodium dioxide.** G. Chancel and E. Diacon observed that **lead dioxide** has no action on tetrathionic acid. Oxidizing agents like **chlorine** transform the acid into sulphate. H. Debus said that **bromine** water gradually added to a tetrathionate soln. results in the separation of sulphur: $K_2S_4O_6+2H_2O+Br_2=2KBr+2H_2SO_4+2S$; the sulphur dissolves in the liquid during stirring, forming penta- and hexa-thionates. M. Berthelot gave for the heat of oxidation ($Na_2S_4O_6.7Br_2Aq.$)=271·0 Cals. The tetrathionates are oxidized by **hypochlorous acid.** M. J. Fordos and A. Gélis, and H. Hertlein found that **hydrochloric acid** does not decompose the acid, but makes it more stable; but if the mixture be warmed, F. Kessler said that hydrogen sulphide is given off. G. S. Jamieson represented the reaction with **iodates:** $2Na_2S_4O_6+7KIO_3+10HCl=4H_2SO_4+2Na_2SO_4+2K_2SO_4+7ICl+3KCl+H_2O$. F. Calzolari represented the reaction with bromates: $HBrO_3+H_2S_4O_6+3H_2O=HBr+3H_2SO_4+H_2S$. The reaction was also studied by F. Fischer and W. F. Tschudin.

According to H. Debus, **sulphur,** *in statu nascendi,* converts the tetrathionates into pentathionates, for instance, potassium tetrathionate in the presence of sulphuric acid, is converted by **hydrogen sulphide** into pentathionate. V. Lewes found that thiosulphate is produced by the action of hydrogen sulphide on a soln. of potassium tetrathionate: $K_2S_4O_6+3H_2S=K_2S_2O_3+3H_2O+5S$, and this reduction is assumed to occur in two stages: $K_2S_4O_6+H_2S=K_2S_2O_3+H_2S_2O_3+S$, and $H_2S_2O_3+2H_2S=3H_2O+4S$. H. Debus found that when an aq. soln. of tetrathionic acid was treated repeatedly with hydrogen sulphide, sulphur and pentathionic acid were formed: $H_2S_4O_6+5H_2S=6H_2O+9S$, and some of the sulphur uniting with the undecomposed tetrathionic acid forms pentathionic acid; but if the treatment with hydrogen sulphide be continued long enough, only water and sulphur are formed. W. Petzold represented the reaction: $2H^{\cdot}+S_3O_6{}''+H_2S=2S_2O_3{}''+4H^{\cdot}+S$. Freshly precipitated **lead sulphide** was found by F. Kessler to react with tetrathionic acid, forming sulphur dioxide. G. Chancel and E. Diacon, and W. Smith and T. Takamatsu said that **potassium sulphide** reacts with a tetrathionate, forming thiosulphate: $K_2S_4O_6+K_2S=2K_2S_2O_3+S$. H. Debus found that tetrathionic acid is reduced by **sulphur dioxide,** forming sulphur and trithionic acid. The sulphur produces thiosulphuric acid which, instead of precipitating sulphur during standing or evaporation of the sulphuric acid, gives half its sulphur to the trithionic acid or the undecomposed tetrathionic acid so as to form tetrathionic and pentathionic acids. W. Spring also observed that tetrathionates are reduced to trithionates by sulphur dioxide—*vide infra,* the action of sulphur dioxide and sulphites on the pentathionic acid. W. Petzold, W. Feld, F. Overdick, and F. Förster and K. Centner represented the reaction: $S_4O_6{}''+SO_3{}''\rightleftharpoons S_3O_6{}''+S_2O_3{}''$. J. E. Mackenzie and H. Marshall found that a pure soln. of potassium tetrathionate decomposes only slowly, with the deposition of sulphur; the deposition of sulphur takes place more rapidly if a small quantity of thiosulphate, or of sulphurous acid, is added to the soln., and still more rapidly if both substances are added. The explanation of this is to be found in the observations made by A. Colefax, that sulphite removes sulphur from tetrathionate with formation of thiosulphate and trithionate: $M_2S_4O_6+M_2SO_3\rightleftharpoons M_2S_2O_3+M_2S_3O_6$. In a soln. which, in addition to the above, contains free sulphurous acid, the action expressed in the following equation will take place: $M_2S_2O_3+H_2SO_3\rightleftharpoons M_2SO_3+H_2S_2O_3$. This is not a stable equilibrium, however, since the sulphite will take up more sulphur from the tetrathionate, and the thiosulphuric acid will decompose with deposition of sulphur and regeneration of sulphurous acid. The presence of thiosulphate and sulphurous acid together in the soln. will therefore greatly accelerate the decomposition of the tetrathionate in the direction of forming trithionate and liberating sulphur. In view of this fact, it is evident that a slight excess of persulphate must be used in the preparation of the tetrathionate. On the other hand, by using an excess of thiosulphate a satisfactory yield of trithionate may be obtained. M. J. Fordos and A. Gélis, and H. Hertlein observed that **sulphuric acid** does not decompose tetrathionic acid, but rather makes it more stable. F. Raschig found that an acidified soln. of **sodium thiosulphate** converts the tetrathionates into pentathionates. According to A. Gutmann, **hydroxylamine** in acidic soln. oxidizes the sulphite residue in tetrathionic acid to sulphuric acid, and is itself reduced to ammonia, $H_2S_4O_6+NH_2.OH+H_2O=2H_2SO_4+2S+NH_3$. In alkaline soln., on the other hand, the loosely combined oxygen atom of the tetrathionate oxidizes hydroxylamine to nitrous or nitric acid, $Na_2S_4O_6+2NH_2.OH+3NaOH=2Na_2S_2O_3+NaNO_2+3H_2O+NH_3$. The reaction was studied by B. Jirgensons. According to M. J. Fordos and A. Gélis, **nitric acid** oxidizes tetrathionic acid to sulphuric acid with the separation of sulphur. A. Gutmann showed that in alkaline soln., **sodium arsenite** reacts with sodium tetrathionate: $3Na_3AsO_3 + Na_2S_4O_6+2NaOH=2Na_2SO_3 +2Na_3AsSO_3+Na_3AsO_4+H_2O$. The reaction was also discussed by T. S. Price and D. F. Twiss, and by J. E. Mackenzie and H. Marshall—*vide supra*, polythionic acids. The reaction between tetrathionates and **potassium cyanide** in alkaline soln., unlike the case with dithionates, is symbolized: $Na_2S_4O_6 + 2KCy + 2NaOH=2KCyS + Na_2SO_4+Na_2SO_3+H_2O$. A. Kurtenacker gave $Na_2S_4O_6+2NaCy+H_2O=NaCyS+Na_2SO_4+2HCy+Na_2S_2O_3$. F. Ishikawa studied the kinetics of the reaction. A. Kurtenacker and A. Fritsch added that the reaction proceeds primarily according to this equation with the formation of thiosulphate. In presence of excess of cyanide, the thiosulphate can react further, with formation of sulphite and thiocyanate. This reaction, however, does not take place in dil. soln. at the ordinary temp., and only slowly and incompletely at the b.p. It becomes quantitative in conc. soln. only after long heating. In alkaline soln. some sulphite, as well as thiosulphate, is formed. F. Ishikawa found the velocity of the reaction: $S_4O_6''+Cy+H_2O=CyS'+SO_4''+S_2O_3''+2H^{\cdot}$ in neutral soln. can be represented by $dx/dt=k_2(a-3x)(b-x)$ because the other reaction is instantaneous. Here a denotes the initial conc. of the potassium cyanide; b, that of the tetrathionate; and x, the number of mols of tetrathionate which have been transformed at the time t. E. Weitz and F. Achterberg obtained salts with benzidine.

W. Spring found that **sodium** amalgam converts potassium tetrathionate into the double thiosulphate: $K_2S_4O_6+2Na=2NaKS_2O_3$; and V. Lewes, that **potassium** amalgam forms thiosulphate and, if the soln. be strongly alkaline, potassium sulphide. According to M. J. Fordos and A. Gélis, an excess of **potassium hydroxide** decomposes a tetrathionate into thiosulphate and sulphite, without the formation of sulphuric acid or sulphur: $2K_2S_4O_6+6KOH=3K_2S_2O_3+2K_2SO_3+3H_2O$. Hence, as emphasized by R. M. Chapin, when sodium tetrathionate, produced in iodine titrations, is allowed to remain in the presence of alkalies or alkaline salts, it is partly converted into sodium thiosulphate and sodium sulphite, thus introducing the possibility of an error in the estimations. While M. J. Fordos and A. Gélis's equation represents the reaction with dil. alkali-lye—say 15 per cent. soln. of sodium, potassium, calcium, strontium, or barium hydroxide—A. Gutmann found that with conc. soln. (1 : 1), there is a side reaction: $3Na_2S_4O_6+12NaOH=3Na_2S_2O_3+5Na_2SO_3+Na_2S+6H_2O$, in which traces of sulphide, sulphite, and thiosulphate -but not sulphate—are formed. V. Lewes confirmed these conclusions, but W. Smith and T. Takamatsu said that purified tetrathionic acid is not decomposed by the alkali-lye. C. J. Thatcher represented the action of cold, dil. alkali-lye at room temp. by $4S_4O_6''+6OH'=5S_2O_3''+2S_3O_6''+3H_2O$, and this is in agreement with the observations of A. Kurtenacker and M. Kaufmann. The equation just indicated is in agreement with the observations of E. H. Riesenfeld and G. W. Feld with boiling alkali-lye. M. Berthelot found that the formation of thiosulphate and sulphite occurs with the evolution of heat; C. J. Thatcher also observed that sodium tetrathionate is hydrolyzed in alkaline soln. forming thiosulphate and trithionate. F. Kessler showed that a boiling soln. of potash-lye converts the trithionate into thiosulphate, sulphite, and sulphide. A. Gutmann said that the action with alkali carbonates is different from what it is with the hydroxides, since in addition to thiosulphate, sulphate is formed instead of sulphite: $4Na_2S_4O_6+5Na_2CO_3=7Na_2S_2O_3+2Na_2SO_4+5CO_2$; or $4S_4O_5=7S_2O_2+2SO_3$. F. Raschig represented the reaction with sodium carbonate: $4Na_2S_4O_6+4Na_2CO_3=6Na_2S_2O_3+Na_2S_3O_6+Na_2SO_4+4CO_2$. F. Kessler said that soln. of the **metal salts**—cupric sulphate, mercurous nitrate, mercuric chloride, and silver nitrate—behave towards tetrathionic acid like they do towards pentathionic acid (*q.v.*), and when sat. with ammonia, are not decomposed. Ammoniacal soln. of silver nitrate or mercuric cyanide give no precipitate. G. Chancel and E. Diacon, and E. H. Riesenfeld and G. W. Feld said that no copper sulphide is precipitated when a soln. of a tetrathionate is boiled with copper sulphate. A. Kurtenacker and A. Fritsch found that when a tetrathionate is boiled for half an hour with a soln. of copper sulphate, copper sulphide is precipitated: $S_4O_6{}''=S_3O_6{}''+S$—*vide* Table XVIII. W. Feld represented the reaction with mercuric chloride: $Na_2S_4O_6+2HgCl_2+2H_2O=Na_2SO_4+2HgCl+H_2SO_4+2HCl+2S$; and A. Sander, $2K_2S_4O_6+3HgCl_2+4H_2O=Hg_3S_2Cl_2+4KCl+4H_2SO_4+2S$. M. J. Fordos and A. Gélis said that aq. soln. of tetrathionic acid gives a white precipitate with stannous chloride. A. Gutmann found that sodium stannite reduces an alkaline soln. of tetrathionate to sodium sulphate, forming sodium metastannate and metasulphostannate. A. Longi and L. Bonavia found that the tetrathionates are oxidized slowly in alkaline soln. by **potassium permanganate.** W. Wardlaw and J. D. Sylvester found that with tervalent **molybdenum salts,** sodium tetrathionate forms a brown precipitate, possibly with the intermediate formation of *molybdenum tetrathionate.*

Tetrathionic acid is dibasic, forming salts, **tetrathionates,** $M_2{}'S_4O_6$, which are usually fairly soluble in water, and are precipitated from aq. soln. by alcohol. H. Marshall prepared **ammonium tetrathionate,** $(NH_4)_2S_4O_6$, from barium thiosulphate and ammonium persulphate: $(NH_4)_2S_2O_3+2BaS_2O_3=2BaSO_4+(NH_4)_2S_4O_6$, and the reaction is attended by the development of much heat. E. Divers and M. Ogawa said that the action of heat is probably the same as it is with ammonium trithionate. J. A. Christiansen obtained *p*-toluoyl tetrathionate. F. Kessler prepared **sodium tetrathionate,** $Na_2S_4O_6$, by oxidizing the thiosulphate with neutral cupric chloride; E. Sonstad, with potassium iodate and hydrochloric acid; and N. von Klobukoff triturated a mixture of iodine and sodium thiosulphate with the smallest possible quantity of water. The syrupy liquid—feebly coloured by a slight excess of iodine—was treated with alcohol, and the precipitated tetrathionate washed with alcohol. F. Kessler said that if tetrathionic acid be neutralized with sodium carbonate, or if lead tetrathionate be so treated, then, sodium sulphate, sulphur and sodium sulphate, and sulphite are formed by the decomposition of the tetrathionate. The heat of formation given by J. Thomsen, and M. Berthelot is 375·8 Cals. A. Villiers said that a *dihydrate,* $Na_2S_4O_6.2H_2O$, is obtained from a cold alkaline soln. of sodium thiosulphate and sulphur dioxide. M. Berthelot gave 9·52 Cals. for the heat of soln. at 10·5. F. Kessler, and H. Hertlein used the iodine process for preparing **potassium tetrathionate,** $K_2S_4O_6$. F. Kessler also obtained it as a precipitate by adding tetrathionic acid to an alcoholic soln. of potassium acetate. According to C. F. Rammelsberg, and A. Fock, the tabular crystals are monoclinic with the axial ratios $a:b:c=0·9285:1:1·2642$, and $\beta=78°\ 28'$. H. Hertlein found that the sp. gr. is 2·2962-2·2965, and the mol. vol. 131·74; while for soln. containing 1·519, 3·725, 7·142, and 13·187 per cent. of the salt, the sp. gr. are, respectively, 1·00950, 1·02341, 1·04560, and 1·08671, and the mol. vol. 115·17, 116·76, 117·78, and 119·47. F. Martin and L. Metz gave 393 Cals.; and J. Thomsen, 395·2 Cals. for the heat of formation; and —12·46 Cals. for the heat of soln. H. Hertlein gave for the sp. refraction 0·2625 with the μ-formula, and 0·1543 with the μ^2-formula for aq. soln. at 20° using Na-light. The corresponding values for the mol. refractions are 79·40, and 46·68. V. J. Sihvonen found maxima in the ultra-red reflection spectrum at 8·6μ, 10·1μ, 16·3μ, and 19·4μ. The properties of the salt have been indicated above. J. Meyer and H. Eggeling prepared **rubidium tetrathionate,** $Rb_2S_4O_6$, by the action of iodine on the thiosulphate. The salt furnishes pyramidal crystals, which are not hygroscopic and are stable. They obtained **cæsium tetrathionate,** $Cs_2S_4O_6$, in a similar way.

G. Chancel and E. Diacon made **cuprous tetrathionate,** $Cu_2S_4O_6.nH_2O$, by the action of cupric sulphate on a soln. of barium tetrathionate. It is decomposed in the cold, rapidly when heated, forming cupric sulphide and sulphuric acid. F. Kessler could not crystallize **cupric tetrathionate,** CuS_4O_6, from its aq. soln. G. Chancel and E. Diacon said that it is not so liable to decompose as the cuprous salt. T. Curtius and F. Henkel neutralized Wackenroder's liquid with copper carbonate, added alcohol, and allowed the oily precipitate to crystallize. If Wackenroder's liquid neutralized with cupric carbonate be mixed with an equal vol. of the untreated liquid and evaporated on the water-bath, copper sulphide separates out. The clear liquid on evaporation over sulphuric acid furnishes pale blue crystals of an acid salt. If the salt be dissolved in alcohol, and precipitated by ether, the salt turns yellow and has a composition like an acidic trithionate. The aq. soln. of the blue acid salt can be evaporated over sulphuric acid without decomposition, but the alcoholic soln. deposits copper sulphide. F. Calzolari prepared **copper tetrapyridinotetrathionate,** $CuS_4O_6.4C_5H_5N$, in fairly stable, dark blue, acicular crystals; and G. T. Morgan and F. H. Burstall, **copper bisethylenediaminotetrathionate,** $[Cu\ en_2]S_4O_6$, in dark purple, rhombic prisms, by carefully concentrating and cooling an aq. soln. of 3·4 grms. of cupric chloride, 2·4 grms. of ethylenediamine, and 6·0 grms. of sodium tetrathionate; the crystals are dried over calcium chloride. The well-defined, prismatic crystals of this complex tetrathionate are permanent in air, but on heating at 160° they decompose with blackening. The aq. soln. is stable even on boiling; silver nitrate gives a white precipitate which darkens rapidly; barium chloride has no effect, sodium hydroxide changes the colour from purple to blue, and mineral acids discharge it. T. Curtius and F. Henkel obtained what they regarded as an acid salt—**cupric hydrotetrathionate,** $Cu(HS_4O_6)_2$—in pale blue crystals. Although ammoniacal silver nitrate gives no precipitate with tetrathionic acid, M. J. Fordos and A. Gélis obtained a white precipitate with silver nitrate. It was thought to be **silver tetrathionate,** but it became yellow in a few seconds, and then turned black.

F. Kessler prepared **strontium tetrathionate,** $SrS_4O_6.6H_2O$, by the methods used for the barium salt, but it is less well precipitated by alcohol from its aq. soln. The aq. soln. on evaporation furnishes thin prismatic crystals although much of the salt is thereby decomposed into strontium sulphate, sulphur, and sulphur dioxide. R. Portillo also found that the *hexahydrate*, precipitated by a mixture of alcohol and ether, is stable in air, but in vacuo it loses $4H_2O$, and especially at 40° to 50°. The dehydration of the *dihydrate* occurs with decomposition at 70°. The sp. gr. of the hexa- and di-hydrates are respectively 2·148 and 2·480 at 25°/4°. The mol. vol. of the water of crystallization is 13·8. The solubility of the strontium salt is less than that of the barium salt at temp. below 27°, and greater at higher temp. The solubilities at 0°, 18°, and 30° are respectively 20, 26·3, and 39 per cent. by weight. The mol. heat of soln. in 1000 mols. of water at 17° is —11·6 Cals. M. J. Fordos and A. Gélis prepared **barium tetrathionate,** $BaS_4O_6.2H_2O$, as indicated above. F. Kessler obtained it by adding an eq. quantity of barium acetate to an aq. soln. of the acid, and precipitated the salt with alcohol. T. Curtius and E. Henkel obtained it from Wackenroder's liquid as indicated above; so did

V. Lewes; while H. Marshall treated barium thiosulphate with a persulphate. The clear, colourless crystals of the salt are dihydrated—only V. Lewes regarded them as trihydrated. E. Mathieu-Plessy said that only one mol. of water is retained by the salt in vacuo. T. Curtius and F. Henkel added that the salt decomposes at 100°–110°; and M. J. Fordos and A. Gélis, that when heated it decomposes into water, sulphur, sulphur dioxide, and barium sulphate. T. Curtius and F. Henkel found that the salt is freely soluble in water, but almost insoluble in alcohol—even when boiling. Small quantities of the soln. can be rapidly heated to a point where on cooling they furnish a crystalline mass, whereas with a slower heating the salt decomposes. If the salt is contaminated with thiosulphate it gives a yellow or black precipitate with silver nitrate. The salt can be freed from thiosulphate by dissolution in a little water—in which the thiosulphate does not dissolve—and precipitation of the tetrathionate by alcohol. R. Portillo saw that the dihydrate is rather stable in air; for it does not lose water at 40° to 50°, but it decomposes above this temp. Aq. soln. are unstable whilst alcoholic soln. are stable at ordinary temp. The sp. gr. is 2·777 at 25°/4°; and the percentage solubilities at 0°, 12·8°, and 27·5° are respectively 26·5, 29·8, and 36. The heat of soln. at 17° in 800 mols. of water is −7 cals. F. Calzolari prepared **magnesium bishexamethylenetetraminotetrathionate,** $MgS_4O_6.2C_6H_{12}N_4.8H_2O$, in colourless, transparent prisms, stable in air, soluble in water. M. J. Fordos and A. Gélis obtained **zinc tetrathionate,** ZnS_4O_6, only in aq. soln. It was also made by F. Ephraim and E. Bolle, who said that **zinc triamminotetrathionate,** $ZnS_4O_6.3NH_3$, is formed by the action of ammonia when in soln., and when dry, the salt has the composition **zinc pentamminotetrathionate,** $ZnS_4O_6.5NH_3$. F. Calzolari prepared **zinc tetramminotetrathionate,** $ZnS_4O_6.4NH_3$, in transparent, colourless crystals; also **zinc tetrapyridinotetrathionate,** $ZnS_4O_6.4C_5H_5N$, in colourless, prismatic crystals; and likewise also **cadmium tetrapyridinotetrathionate,** $CdS_4O_6.4C_5H_5N$. T. Curtius and F. Henkel prepared the acid zinc salt, **zinc hydrotetrathionate,** $Zn(HS_4O_6)_2$, as in the case of the copper salt. The evaporation of the aq. soln. furnishes aggregates of small needles, which decompose at 100°. The crystals are hygroscopic; they readily dissolve in water and in alcohol. The conc., aq. soln. forms sulphur when treated with alkali-lye in the cold. The salt is decomposed by mineral acids. F. Kessler obtained **cadmium tetrathionate,** CdS_4O_6, as a deliquescent mass of crystals from a mixed soln. of lead tetrathionate and cadmium sulphate. M. J. Fordos and A. Gélis, and F. Kessler obtained **lead tetrathionate,** PbS_4O_6, from a soln. of lead thiosulphate and iodine; G. Chancel and E. Diacon, by adding sulphuric acid to water with a mixture of lead thiosulphate and dioxide in suspension—A. Chwala and H. Colle employed a somewhat similar process; G. Chancel and E. Diacon, by the action of lead dioxide on a soln. of pentathionic acid; and F. Kessler, by the action of a soln. of lead acetate on a conc. soln. of tetrathionic acid, followed by the addition of alcohol. The salt appears in tabular crystals; the evaporation of the aq. soln. in vacuo is attended by the decomposition of some of the salt into sulphur, and lead sulphate and thiosulphate. A. and P. Lumière and A. Seyewetz found that the soln. in sodium thiosulphate is unstable. W. Wardlaw and N. D. Sylvester obtained evidence of the temporary formation of **molybdenum tetrathionate** by the action of sodium tetrathionate on a soln. of tervalent molybdenum in $3N$-H_2SO_4. T. Curtius and F. Henkel prepared **manganese hydrotetrathionate,** $Mn(HS_4O_6)_2$, by the method employed for the cupric salt (*q.v.*). The aggregates of acicular and tabular crystals are rose-red in colour, and, according to T. Curtius, they can be preserved without change, but decompose at 100° with the formation of sulphur dioxide, hydrogen sulphide, and sulphur. F. Kessler prepared **nickel tetrathionate,** NiS_4O_6, as in the case of the cadmium salt. F. Calzolari prepared **nickel hexamminotetrathionate,** $NiS_4O_6.6HN_3$, in minute, lilac crystals; **nickel tetrapyridinotetrathionate,** $NiS_4O_6.4C_5H_5N$, in blue acicular crystals; **cobalt tetrapyridinotetrathionate,**

$CoS_4O_6.4C_5H_5N$, in violet-red, microscopic needles; **nickel bishexamethylenediaminotetrathionate,** $NiS_4O_6.2C_6H_{12}N_4.8H_2O$, in pale green, transparent prisms; and **cobalt bishexamethylenediaminetetrathionate,** $CoS_4O_6.2C_6H_{12}N_4.8H_2O$, in red prisms, stable in air and soluble in water. C. Perrier studied the crystals of nickel bishexamethylenediaminotetrathionate.

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§ 44. Pentathionic Acid and the Pentathionates

In 1846, H. W. F. Wackenroder,[1] in his memoir: *Ueber eine neue Säure des Schwefels*, described the probable formation of **pentathionic acid,** $H_2S_5O_6$, as a product of the action of hydrogen sulphide on sulphurous acid. The resulting liquid, afterwards known as *Wackenroder's liquid* (*q.v.*), is really sulphurous acid saturated with hydrogen sulphide. H. W. F. Wackenroder then placed plates of polished copper in the liquid, and renewed them from time to time until they were no longer blackened, but retained their polished surface after some hours' immersion in the liquid. The soln. was then supposed to be an aq. soln. of pentathionic acid formed by the reactions $5SO_2+5H_2S=H_2S_5O_6+4H_2O+5S$. The dil. soln. of the acid so obtained is clear, colourless, and without smell. F. Kessler prepared pentathionic acid by saturating sulphurous acid with hydrogen sulphide; digesting the filtered liquid with freshly prepared barium carbonate to remove the sulphuric acid, and evaporating the filtered liquid on a water-bath to a sp. gr. 1·25 or 1·30. F. Kessler said that the acid liquid can be evaporated in vacuo to a sp. gr. 1·6 at 22°; and H. W. F. Wackenroder said that it can be concentrated to a sp. gr. 1·37 without decomposition. H. Debus added that the soln. so prepared is really a mixture of polythionic acids. If a soln. of pentathionic acid alone is required, it can be obtained by treating potassium pentathionate with tartaric acid, and after a couple of days filtering off the potassium tartrate. The soln. will contain a little tartaric acid.

C. Ludwig obtained pentathionic acid by the action of sulphurous acid on hydrogen persulphide; and H. Risler-Beunat, by the action of zinc on sulphurous acid. It is possible that in the latter case there is some confusion with hyposulphurous acid (*q.v.*). G. Chancel and E. Diacon, and G. Vortmann observed that pentathionic acid is formed when thiosulphates are decomposed by acids; F. Raschig, by the action of an acidified soln. of thiosulphate on tetrathionates; J. Persoz, when lead thiosulphate is decomposed by hydrogen sulphide; W. Smith and T. Takamatsu, when lead thiosulphate is decomposed by hydriodic acid and iodine: $3PbS_2O_3+2HI+2I_2=H_2S_5O_6+3PbI_2+SO_3$—W. Spring said that this reaction furnished not pentathionic acid, but a mixture of sulphur, tetrathionic acid, sulphuric acid, and sulphur dioxide. T. Salzer found that pentathionic acid is formed by adding potassium selenite to a soln. of sodium thiosulphate, and treating the product with an excess of hydrochloric acid. G. Vortmann observed pentathionic acid among the products of the action of arsenic acid on sodium thiosulphate. W. Petzold observed that in acidic soln., thiosulphates polymerize to pentathionates $5S_2O_3''+10H^{\cdot}\rightarrow 2S_5O_6''+4H^{\cdot}+3H_2O$. H. Bassett and R. G. Durrant found that when copper chloride, sulphate or nitrate, is treated with excess of sodium thiosulphate in presence of any mineral acid, there is evidence to show that pentathionic acid is produced and remains in soln. after cuprous sulphide and excess of sulphur have been thrown out by boiling. This must be due to interaction between sodium tetrathionate, sodium thiosulphate, and the mineral acid: $Na_2S_4O_6+Na_2S_2O_3+4HA'=H_2S_5O_6+4NaA'+H_2O+SO_2$. When vapours of water and sulphur are passed through a red-hot tube, E. Gripon observed that some pentathionic acid is formed; and J. Myers, when steam is passed over molten sulphur; and T. Brugnatelli and P. Pelloggio found that when sulphur oxidizes in the presence of air and moisture sulphuric acid is first formed, and afterwards pentathionic acid—*vide supra*, sulphur. M. J. Fordos and A. Gélis, and E. Mathieu-Plessy said pentathionic acid is formed when water acts on sulphur mono- or di-chloride: $5S_2Cl_2+6H_2O=5S+10HCl+H_2S_5O_6$. H. Debus showed that a mixture of tri-, tetra-, and penta-thionic acid is formed—*vide supra*, trithionic acid. J. S. Maclaurin found 0·024 per cent. of pentathionic acid in the water from a lake on the summit of a volcano on White Island, New Zealand, and added that it may have been missed in many analyses because no special search was made for it.

The salts of pentathionic acid are not so easily prepared. H. W. F. Wackenroder could not prepare them by neutralizing pentathionic acid with strong bases, because the acid is decomposed by that treatment; and F. Kessler obtained only a mixture of tetrathionate and sulphur in this way. C. Ludwig divided Wackenroder's liquid into two equal parts, neutralized one part with potassium carbonate, and mixed it with the other part. The evaporation of the liquid gave what was regarded as a mixture of penta- and tetra-thionates. According to G. A. Lenoir, crystals of barium pentathionate are produced from the liquid obtained by treating Wackenroder's liquid with barium carbonate by treating it with alcohol, or, according to M. J. Fordos and A. Gélis, with alcoholic ether; but T. Curtius said that if pentathionic acid be neutralized with barium carbonate, and the liquid poured into alcohol, barium tetrathionate is formed: $BaCO_3+H_2S_5O_6=BaS_4O_6+S+H_2O+CO_2$. H. Debus said that the product obtained by G. A. Lenoir's process from Wackenroder's liquid varies in composition with the quantity and concentration of the alcoholic soln. As indicated below, pentathionic acid is decomposed by an excess of alkali-lye.

As a result of these difficulties in preparing the pentathionates, W. Spring was led to question the existence of pentathionic acid as a chemical individual. He regarded what was considered to be pentathionic acid as a soln. of sulphur in tetrathionic acid. W. Smith and T. Takamatsu, and V. Lewes tried to demonstrate the existence of pentathionic acid in Wackenroder's liquid, by treating it with mercuric cyanide, $H_2S_5O_6+HgCy_2+2H_2O=2H_2SO_4+HgS+2HCy+2S$, and finding the proportions of sulphuric acid, mercuric sulphide, and sulphur in the product. They found the molar ratio 2 : 1 : 2; tetrathionic acid would give a ratio 2 : 1 : 1. As H. Debus emphasized, this does not demonstrate the existence of pentathionic acid. This was done when V. Lewes prepared and analyzed the solid potassium pentathionate. V. Lewes added to a portion of Wackenroder's liquid about half the quantity of potassium hydroxide required for complete neutralization; sulphur was precipitated during the operation, and the filtrate on spontaneous evaporation, furnished as a first crop crystals of potassium tetrathionate; this was followed by crystals of hydrated potassium pentathionate, which were purified by recrystallization from water acidified with sulphuric acid, which hinders the decomposition which occurs when water alone is employed as solvent. If baryta-water be used, the first crop of crystals consists of barium tetrathionate; there follows a mixture of tetra- and penta-thionates; and finally the pentathionate. This was confirmed by S. Shaw; although W. Spring maintained that V. Lewes's crystals were impure. H. Debus avoided the decomposition of the acid by free bases by neutralizing Wackenroder's liquid with acetates. This process is as follows:

Forty-three c.c. of Wackenroder's liquid of sp. gr. 1·343 containing about 24 grms. of pentathionic acid were mixed with 16·6 grms. of potassium acetate dissolved in the smallest quantity of water and acidulated with a few drops of acetic acid. A current of air was passed over the surface of the liquid, and in 24 hrs., 26 grms. of a white, crystalline residue were obtained. This was pressed between bibulous paper, and dissolved in 50 c.c. of water acidulated with one c.c. of sulphuric acid at 40°. The filtered liquid was allowed to evaporate spontaneously, and it furnished 18 grms. of a mixture of potassium tetra- and penta-thionates—5·75 grms. of potassium pentathionate were picked from the mixture. This and the residue were separately recrystallized from water acidulated with sulphuric acid—2·25 grms. of water and 0·02 grm. of acid were used for each gram of salt. The crystals of pentathionate were separated by hand-picking. In this way a yield of 5 grms. of potassium pentathionate and 6·35 grms. of the tetrathionate were obtained of a high degree of purity. The pentathionates of other metals were produced by adding their acetates to Wackenroder's liquid in a similar manner.

A. Fock and K. Klüss employed a similar process. F. Raschig obtained the acid by the action of hydrochloric acid (200 c.c. of acid of sp. gr. 1·18) at −10° on an aq. soln. of sodium thiosulphate (125 grms. of crystals with 150 c.c. of water) at −10°, and 2·5 grms. of arsenic trioxide dissolved in the smallest possible quantity of sodium hydroxide. Sodium pentathionate gradually separates on concentrating the filtrate at 35°. The filtrate still contains 12 per cent. of sodium pentathionate and 60 per cent. of pentathionic acid free from tri- or tetra-thionic acids, and it can be kept 2 months with scarcely any change. The presence of arsenic, antimony, or tin salts prevents the separation of sulphur on acidifying soln. of sodium thiosulphate: $Na_2S_2O_3+2HCl \rightarrow 2NaCl+SO_2+S$; and with sodium hydroarsenite instead of 88 per cent., only 13 per cent. was so reduced, while 85 to 90 per cent. of pentathionate was formed. It was assumed that in forming pentathionic acid from sodium thiosulphate, the latter furnishes the group $S:SO_2$ which polymerizes to $S_{10}O_{10}$, so that the dipentathionate, $H_4S_{10}O_{12}$, is supposed to be formed as an intermediate compound—*vide supra*, polythionic acid. F. Raschig prepared the potassium salt in an analogous way. H. Hertlein separated the alkali tetra- and penta-thionates by treating the crystalline product with a mixture of xylene and bromoform of sp. gr. 2·2—the tetrathionate sinks while the pentathionate floats.

Pentathionic acid is known only in aq. soln., and **pentathionic anhydride,** S_5O_5, has not been prepared. The aq. soln. is colourless, free from smell, and has a strongly acid and bitter taste. The soln., said H. W. F. Wackenroder, can be preserved unchanged at ordinary temp., although, according to M. J. Fordos and A. Gélis, it gradually decomposes into tetra- and tri-thionic acids and sulphur. The presence of acids makes it more stable. When the conc. aq. soln. is boiled, H. W. F. Wackenroder found that the aq. soln. decomposes into hydrogen sulphide and sulphurous and sulphuric acids; and F. Kessler added that only the conc. acid soln. gives off sulphur dioxide when boiled. For the hydrolysis of pentathionic acid, *vide supra*, tetrathionic acid. According to W. Petzold, the pentathionates decompose when heated, forming tetrathionate and sulphur; and a similar decomposition occurs in aq. soln. There is also a state of equilibrium: $S_5O_6''+2S_2O_3'' \rightleftharpoons 2S_4O_6''+S$. H. Debus found that the pentathionates are easily soluble in water, but insoluble in alcohol. The aq. soln. decomposes on keeping with the separation of sulphur. Hydrochloric and sulphuric acids retard the decomposition of the aq. soln., and acetic acid favours it. A 10 per cent. soln. of potassium pentathionate can be boiled for a long time without decomposition, but hydrogen sulphide is formed and some sulphur deposited. A. Gutmann said that a boiling aq. soln. of sodium tetrathionate forms sodium sulphate, sulphur dioxide, and sulphur, not trithionate and sulphur as stated by F. Kessler. W. Smith, and H. Debus noticed that while pentathionic acid is fairly stable, the salts are unstable. E. H. Riesenfeld and G. W. Feld attempted to explain this by inventing " the hydrate of SO " theory which is supposed to be stable, and to polymerize to produce pentathionic acid. H. Debus assumed an analogous S_2O_2, where $5S_2O_2=2S_5O_5$, and $H_2O+S_5O_5=H_2S_5O_6$. H. Bassett and R. G. Durrant assume that the molecule of pentathionic acid is stable while the pentathionic-anion is unstable; and that the salts are unstable because they tend to ionize under conditions in which the acid does not ionize. They added that any reagent that develops alkalinity immediately precipitates sulphur from pentathionic acid (salt formation). Soln. containing pentathionic acid in a slight excess of mineral acid slowly decompose in the cold with formation of sulphuric acid, deposition of sulphur, and evolution of sulphur dioxide, but in fairly conc. mineral acid the soln. may be boiled for several hours without separation of sulphur. According to F. Kessler, aq. soln. with 32·1, 41·7, 56·0, and 59·7 per cent. S_5O_5 have a sp. gr. 1·233, 1·320, 1·474, and 1·506 respectively. H. Debus said that these numbers are only approximate. J. Thomsen gave for the heat of formation (5S,5O,Aq.)=133·11 Cals., and M. Berthelot, 215·8 Cals. H. Hertlein gave for the transport number, $\frac{1}{2}S_5O_6$, 61·4 at 25°.

H. W. F. Wackenroder found that **chlorine** and **hypochlorous acid** oxidize pentathionic acid to sulphuric acid; and M. J. Fordos and A. Gélis gave $BaS_5O_6+10H_2O+10Cl_2=BaSO_4+4SO_3+20HCl$. F. Kessler added that when chlorine is passed into the liquid, some hydrogen sulphide is given off, and sulphur deposited; while boiling **hydrochloric acid** liberates some hydrogen sulphide. The preserving action of hydrochloric acid has been already indicated. H. Debus observed no perceptible change when hydrochloric acid is added to a soln. of potassium pentathionate. M. Berthelot said that **bromine** oxidizes pentathionates to sulphates, and the heat developed ($K_2S_5O_6,10Br_2aq.$)=362·6 Cals. H. Debus found that bromine removes two atoms of sulphur from pentathionates, and that an **iodine** soln. is decolorized by pentathionic acid in 24 hrs. F. Raschig observed that a mixture of **potassium chlorate** and hydrochloric acid oxidizes pentathionic acid to sulphuric acid. According to H. W. F. Wackenroder, **hydrogen sulphide** does not decompose the acid, but G. Chancel and E. Diacon observed that the acid is decomposed with the separation of sulphur; and H. Debus showed that by repeated treatment with hydrogen sulphide, the acid can be completely decomposed: $H_2S_5O_6+5H_2S=6H_2O+10S$; and a soln. of potassium pentathionate decomposes as indicated by the equation: $3K_2S_5O_6+3H_2S=K_2S_2O_3+2K_2S_3O_6+3H_2O+10S$. W. Petzold represented the reaction: $2H^{\cdot}+S_5O_6''+H_2S=2S_2O_3''+4H^{\cdot}+2S$. H. W. F. Wackenroder said that the **sulphur dioxide** decomposes a conc. soln. of the acid; and H. Debus showed that an excess of sulphur dioxide transforms a portion of a soln. of the acid into tetra- or tri-thionic acid, and part remains undecomposed, while pentathionates are completely transformed into trithionates and thiosulphates; with neutral soln. of **sulphites** some sulphur dioxide is given off, and sulphur deposited. The reaction was studied by W. Feld, and F. Overdick. According to F. Fôrster and K. Centner, the action of sulphites on tetrathionates and pentathionates, with the sulphite in slight excess, are complete reactions: $S_5O_6''+SO_3''\rightarrow S_4O_6''+S_2O_3''$, in which the velocity constant $k=0{\cdot}233$ with time in minutes and concentration in millimols; and $S_4O_6''+SO_3''\rightarrow S_3O_6''+S_2O_3''$, in which the velocity constant $k=0{\cdot}0103$. If the eq. proportions are present, the reactions are balanced ones: $S_5O_6''+SO_3''\rightleftharpoons S_4O_6''+S_2O_3''$, and $S_4O_6''+SO_3''\rightleftharpoons S_3O_6''+S_2O_3''$, in which the right-side reactants are dominant; and there is also involved the equilibrium $2S_4O_6''\rightleftharpoons S_5O_6''+S_3O_6''$, which is catalyzed by the S_2O_3''-ions. With hydrosulphites, the equilibria $S_5O_6''+HSO_3'\rightleftharpoons S_4O_6''+S_2O_3''+H^{\cdot}$, and $S_4O_6''+HSO_3'\rightleftharpoons S_3O_6''+S_2O_3''+H^{\cdot}$, are only slowly attained. At the beginning of the reaction with hydrosulphites the velocity constants at 0° are about the same as with the sulphites; and for the same polythionates, the velocity at the beginning of the reaction with the hydrosulphites is to that with the sulphites in the ratio of the conc. of the SO_3''- and HSO_3'-ions in the state of equilibrium: $HSO_3'\rightleftharpoons H^{\cdot}+SO_3''$. Hence, it is inferred that in a soln. of hydrosulphite, only the contained SO_3''-ions are active. There is also the secondary reaction $S_3O_6''+H_2O=SO_4''+S_2O_3''+2H^{\cdot}$. The equilibrium with hydrosulphite and pentathionate is more rapidly attained than it is with tetrathionate, and with not too great an excess of hydrosulphite; the decomposition of the tetrathionate into thiosulphate occurs as a consecutive reaction after the equilibrium is attained. The pentathionate produced by the action of $H^{\cdot}$-ions on S_2O_3''-ions can therefore be more rapidly converted to tetrathionate by hydrosulphite. The trithionate can also be formed by the action of the hydrosulphite: $S_2O_3''+4HSO_3'+2H^{\cdot}\rightarrow 2S_3O_6''+3H_2O$. The thiosulphate is also broken down by the reactions symbolized: $S_2O_3''+H^{\cdot}\rightarrow HSO_3+S$; and $S_2O_3''+2HSO_3\rightarrow 2SO_4''+2S+H_2O$, where the trithionate ions act as a catalyst. W. Petzold represented the reaction: $S_5O_6''+2SO_3''\rightleftharpoons S_3O_6''+2S_2O_3''$; and F. Förster and K. Centner, $S_5O_6''+SO_3''\rightleftharpoons S_4O_6''+S_2O_3''$, and with tetrathionates, $S_4O_6''+SO_3''\rightleftharpoons S_3O_6''+S_2O_3''$. If, however, a slight excess of sulphite is present, both reactions are completed to the right in accordance with the ordinary bimolecular law, the speed of the former reaction being much greater than that of the latter. When a hydrosulphite acts on a pentathionate and tetrathionate, the equilibria $S_5O_6''+HSO_3'\rightleftharpoons S_4O_6''+S_2O_3''+H^{\cdot}$ and $S_4O_6''+HSO_3'\rightleftharpoons S_3O_6+S_2O_3''+H^{\cdot}$ are slowly established, the reactions probably being brought about entirely by the sulphite ions present in the hydrosulphite soln. The second equilibrium is disturbed by the decomposition of the trithionate, according to the equation $S_3O_6''+H_2O=SO_4''+S_2O_3''+2H^{\cdot}$, and by its re-formation from hydrosulphite and thiosulphate, $S_2O_3''+4HSO_3'+2H^{\cdot}=2S_3O_6''+3H_2O$. As a result of these reactions, the hydrogen-ion conc. increases until sulphur is deposited by the reaction

$S_2O_3''+H^{\cdot}\rightleftharpoons HSO_3'+S$. Finally, a stationary state is reached, and sulphate and free sulphur are formed from thiosulphate and sulphite, corresponding with the equation $S_2O_3''+2HSO_3'=2SO_4''+2S+H_2O$. Since a hydrosulphite and free sulphur can be obtained from thiosulphate by the action of acids, thiosulphate itself can, under suitable conditions of acidity, be converted into sulphate and sulphur. A. Kurtenacker and M. Kaufmann said that **trithionates** do not react with pentathionates to form tetrathionates: $S_3O_6''+S_5O_6''=2S_4O_6$, even in acidic soln., but trithionates and their decomposition products accelerate the decomposition of pentathionate to tetrathionate and sulphur. The preserving action of dil. **sulphuric acid** has been just indicated. H. Debus found that **ammonia** after a few minutes makes pentathionic acid turbid, probably owing to the separation of sulphur; H. Debus, and F. Kessler noticed that if ammonia be added to a soln. of a pentathionate, and then hydrogen sulphide, there is a copious deposit of sulphur. H. W. F. Wackenroder said that **nitric acid** oxidizes the acid to sulphate; while **phosphine** does not decompose the acid. E. Wertz and F. Achterberg obtained some benzidine salts.

H. W. F. Wackenroder observed that the acid exerts no action on polished strips of copper, but when boiled with **copper,** pentathionic acid decomposes, forming sulphur dioxide, sulphuric acid, and copper sulphide; and when boiled with **iron,** hydrogen sulphide is evolved and ferrous sulphate and thiosulphate are formed. H. Debus said that plates of copper or **silver** are blackened by a soln. of potassium pentathionate. V. Lewes observed that with **potassium** amalgam pentathionates are reduced to tetrathionate, then to thiosulphates, and finally to hydrogen sulphide. H. Debus showed that when shaken with **platinum** black, a soln. of pentathionate becomes acidic owing to the formation of sulphuric acid, but no sulphur is deposited.

According to M. J. Fordos and A. Gélis, and M. Berthelot, an excess of **alkali hydroxide** immediately decomposes pentathionic acid: $2K_2S_5O_6+6KOH=5K_2S_2O_3+3H_2O$; J. Stingl and T. Morawsky said that **alkali carbonates** or hydroxides, or the **alkaline earth hydroxides or carbonates,** in the cold, decompose pentathionic acid, forming tetrathionic acid, and if heated, trithionic acid and sulphur are formed. W. Smith and T. Takamatsu also noticed that when exactly neutralized with potassium hydroxide, pentathionic acid forms tetrathionate and sulphur; and with more alkali hydroxide, sulphur, sulphite, and thiosulphate are formed: $2H_2S_5O_6+10KOH=3S+3K_2SO_3+2K_2S_2O_3+7H_2O$. T. Curtius also found that baryta-water, or freshly precipitated barium carbonate, converts pentathionic acid into tetrathionate and sulphur: $H_2S_5O_6+BaCO_3=BaS_4O_6+S+H_2O+CO_2$. V. Lewes represented the reaction with pentathionates and alkali-lye in excess: $2K_2S_5O_6+6KOH=3K_2S_2O_3+2K_2SO_3+3H_2O+2S$. W. Smith and T. Takamatsu employed an equation analogous to that indicated above for the acid. V. Lewes said that when a pentathionate is warmed with alkali hydroxide, sulphur and trithionate are formed, and when boiled, thiosulphate is produced: $2K_2S_5O_6+6KOH=5K_2S_2O_3+3H_2O$. This is also in agreement with the observations of E. H. Riesenfeld and G. W. Feld. A. Kurtenacker and M. Kaufmann said that the primary reaction with cold, dil. alkali-lye is: $S_5O_6''\rightleftharpoons S+S_4O_6''$; and the tetrathionate then decomposes: $2S_4O_6''+6OH'=3S_2O_3''+2SO_3''+3H_2O$, and $2SO_3''+2S_4O_6''=2S_3O_6+2S_2O_3''$, that is, according to $4S_4O_6''+6OH'=5S_2O_3''+2S_3O_6''+3H_2O$. The sulphur which redissolves may react with some of the sulphite: $S+SO_3''=S_2O_3''$, or more probably with an excess of alkali, $4S+6OH'=2S''+S_2O_3''+3H_2O$; and the sulphide then reacts with the trithionate: $S_3O_6+S=2S_2O_3$; so that the resultant reaction is $2S_5O_6''+6OH' \quad 5S_2O_3''+3H_2O$. Boiling, conc. alkali-lye decomposes pentathionates, forming sulphides. F. Raschig said that under suitable conditions *one* atom of sulphur separates from the pentathionates on treatment with **sodium carbonate,** and the reaction $K_2S_5O_6\rightarrow K_2S_4O_6+S$ is quantitative. A. Kurtenacker and A. Czernotzky, however, found that the reaction goes far beyond this stage in dil. soln.

According to H. W. F. Wackenroder, **cupric sulphate** when boiled for some time with pentathionic acid gives a brown precipitate; while H. Debus said that **cupric chloride, acetate, and sulphate** cause no change with soln. of potassium pentathionate. F. Kessler, and H. W. F. Wackenroder observed that **silver nitrate** gives a yellow precipitate which soon turns black; and F. Kessler said that an ammoniacal soln. of silver nitrate gives with a soln. of pentathionate first a brown precipitate and this passes into black silver sulphide. H. Debus added that this reaction is not produced by a soln. of tri- or tetra-thionate, thiosulphate, or sulphite, for an ammoniacal soln. of silver nitrate seems to have no effect on these salts. Consequently, a pentathionate, even if present in very small quantity, can be detected in a mixture of potassium tri- and tetra-thionates and sodium, potassium, and ammonium thiosulphates. A soln. of **barium chloride,** or **zinc sulphate,** causes no visible change in a soln. of potassium pentathionate. H. W. F. Wackenroder, and F. Kessler said that with pentathionic acid, **mercurous nitrate** gives a yellow precipitate which when exposed to light or boiled becomes black; with an excess of the mercury salt, the precipitate is white and remains white; while **mercuric nitrate, chloride, or cyanide** gives a white or yellow precipitate which gradually blackens in the cold, and rapidly when heated. F. Kessler, and H. Debus said that an ammoniacal soln. of mercuric cyanide produces a black precipitate with potassium pentathionate—gradually in the cold, rapidly at 100°. H. Debus observed that mercuric cyanide removes two atoms of sulphur from pentathionates, and A. Sander, that mercuric chloride acts similarly. E. H. Riesenfeld and G. W. Feld represented the reaction: $2S_5O_6''+2Hg''+4H_2O=2HgS+4SO_4''+8H^{\cdot}+4S$. All the polythionic acids are decomposed by a mercuric salt in neutral soln. H. W. F. Wackenroder found that **stannous chloride** with pentathionic acid gives a white precipitate which gradually turns yellow; and F. Kessler said that with pentathionates, stannous chloride gives a chocolate precipitate. H. Debus observed no visible change on adding soln. of **lead nitrate or acetate, ferric chloride,** or **cobalt nitrate** to a soln. of potassium pentathionate; a soln. of **potassium permanganate** gives a coffee-brown precipitate. F. Raschig said that pentathionic acid is slowly oxidized by an acidic soln. of potassium permanganate. M. J. Fordos and A. Gélis said that in acidic soln. potassium permanganate is reduced by barium pentathionate—*vide* Table XVIII. J. J. P. Valeton said that the ordinary tests employed to distinguish pentathionic acid from the other polythionic acids—the action of strong bases, ammonia, ammoniacal mercuric cyanide, ammoniacal silver nitrate, and ammonia followed by hydrogen sulphide—are valueless, since a pure colloidal soln. of sulphur reacts similarly, and all these alkaline reagents decompose pentathionic acid with precipitation of sulphur. There is no test applicable to the detection of pentathionic acid in aq. soln. H. Bassett and R. G. Durrant agree that the positive tests given by H. Debus for pentathionic acid—(i) darkening of an ammoniacal soln. of silver nitrate; (ii) deposition of sulphur with alkali-lye; (iii) rapid deposition of sulphur with aq. ammonia; (iv) immediate deposit of sulphur with aq. ammonia containing hydrogen sulphide; and (v) black precipitate with an ammoniacal soln. of mercuric cyanide—are given by colloidal sulphur, but the negative tests—no precipitate with hydrochloric acid, cupric chloride, acetate, or sulphate, ferric chloride, or cobalt nitrate—gave precipitates with colloidal sulphur. The most delicate distinguishing test is didymium chloride; the merest trace of the tervalent cation precipitated sulphur from the colloidal soln., but a considerable amount failed to have any effect on pentathionic acid. Pentathionic acid, therefore, is unaffected by electrolytes provided the soln. is not rendered alkaline. In this respect, it differs from colloidal sulphur. Another way to differentiate them is to boil each for a short time with hydrochloric acid and then apply Debus's "positive" tests involving alkali. It will be found that pentathionic acid responds to all the tests, and what *was* colloidal sulphur to none of them. J. J. P. Valeton's statement may be modified by saying that pentathionic acid, when rendered alkaline, liberates colloidal sulphur.

Pentathionic acid is dibasic, furnishing salts, the **pentathionates,** $M_2'S_5O_6$.

Owing to its instability, **sodium pentathionate,** $Na_2S_5O_6$, has not been examined except in aq. soln., but, as previously shown, F. Raschig obtained crystals of the salt. As indicated above, **potassium pentathionate,** $K_2S_5O_6.1\frac{1}{2}H_2O$, cannot be obtained in a satisfactory way by neutralizing the acid with the alkali hydroxide owing to its conversion into the tetrathionate. The preparation of the pentathionate has been previously described. It was made by T. Curtius, C. Ludwig, V. Lewes, A. Fock and K. Klüss, H. Debus, F. Raschig, H. Hertlein, etc. S. Shaw supposed that the salt is a monohydrate; V. Lewes, a dihydrate; and H. Debus, a hemitrihydrate. The crystals described by C. F. Rammelsberg were probably those of a tetrathionate. According to A. Fock and K. Klüss, the colourless rhombic crystals have the axial ratios $a:b:c=0·4564:1:0·3051$. H. Hertlein gave 2·1120–2·1126 for the sp. gr., and 171·19 for the mol. vol. The sp. gr. of aq. soln. containing 1·671, 4·082, 7·723, and 14·199 per cent. of the salt are 1·01002, 1·02467, 1·04740, and 1·009025 respectively at 20°, and the mol. vol. respectively 135·95, 137·25, 138·51, and 139·53. F. Martin and L. Metz gave 386 Cals. for the heat of formation of $K_2S_5O_6$; and M. Berthelot gave for the heat of formation from its elements, in aq. soln., 203·5 Cals.; for the heat of oxidation by bromine, 19·5 Cals.; and for the reaction with potassium hydroxide, 24·10 Cals. H. Hertlein found the sp. refraction with the μ-formula to be 0·2837 at 20° for Na-light, and with the μ^2-formula, 0·1665; while the mol. refractions are respectively 94·92 and 55·73. The electrical conductivity of a soln. of a mol of the salt in v litres of water at 25° was found to be:

v .	32	64	128	256	512	1025
μ .	106·2	112·3	117·7	122·2	125·7	129·3

According to H. Debus, the crystals of potassium pentathionate cannot be kept long. In the course of a month or two, yellow points are observed in them; these points grow and increase in number, until the whole crystal is turned into a yellow, pulpy mass consisting chiefly of water, potassium tetrathionate, and sulphur. The cause of this spontaneous decomposition is the presence of water contained in cracks and fissures of the crystals. In order to preserve the salt, the crystals must be rubbed to a fine powder and the latter washed with dil. alcohol. In this state, the salt can be kept over sulphuric acid in a desiccator for two or three years without the slightest change. According to V. Lewes, and S. Shaw, when the pentathionate is heated, it decomposes into sulphate, etc., $2K_2S_5O_6=2K_2SO_4+2SO_2+6S$. Potassium pentathionate is easily soluble in water—100 parts of water dissolving about 50 parts of salt—but it is not soluble in alcohol. The properties of the salt have been previously discusssed. J. A. Christiansen prepared *p-toluoyl pentathionate.*

H. Debus reported **copper pentathionate,** $CuS_5O_6.4H_2O$, to be formed by mixing 20 grms. of cupric acetate dissolved in 250 c.c. of water, with 45 c.c. of Wackenroder's liquid of sp. gr. 1·325, and allowing the soln. to evaporate spontaneously; the product was dried between bibulous paper, and recrystallized from its aq. soln. The blue, prismatic crystals are freely soluble in water; and they decompose when kept, forming brown cupric sulphide and sulphur. G. T. Morgan and F. H. Burstall's attempt to prepare an ethylenediaminopentathionate was unsuccessful, owing to the destructive action of the diamine in removing sulphur from the alkali pentathionates obtained from Wackenroder's soln. M. J. Fordos and A. Gélis, G. A. Lenoir, and V. Lewes prepared **barium pentathionate,** $BaS_5O_6.2H_2O$, as indicated above. V. Lewes prepared it as a trihydrate. The clear, colourless prisms were stated by G. A. Lenoir to be tetragonal. When heated in a tube, the salt decomposes into sulphur, sulphur dioxide, and hydrogen sulphide; and the dry salt, at 100°, was found by V. Lewes to decompose: $BaS_5O_6.3H_2O=BaSO_4+SO_2+3S+3H_2O$. The salt was found by M. J. Fordos and A. Gélis, and V. Lewes to be freely soluble in water, and insoluble in alcohol. A mixture of tetrathionate and pentathionate was obtained by M. J. Fordos and A. Gélis, C. Ludwig, F. Kessler, and V. Lewes; and it was called barium tetrapentathionate, $BaS_9O_{12}.6H_2O$, *i.e.* $BaS_4O_6.BaS_5O_6.6H_2O$. H. Debus prepared impure **zinc pentathionate,** by the method used for the copper salt. The soln. is very unstable, and most of it decomposes into sulphate on evaporation. A. and P. Lumière and A. Seyewetz obtained a soln. of **lead pentathionate,** PbS_5O_6, by neutralizing an aq. soln. of pentathionic acid with lead carbonate, and with a soln. of sodium thiosulphate it appears to form lead sulphite, sulphur, and **sodium lead pentathionate,** $Na_2Pb(S_5O_6)_2$.

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§ 45. Hexathionic Acid and the Hexathionates

H. Debus[1] said that the mother-liquor remaining after the separation of potassium tetra- and penta-thionates from Wackenroder's liquid—*vide supra*—contains the potassium salt of **hexathionic acid,** $H_2S_6O_6$. He obtained **potassium hexathionate,** $K_2S_6O_6.1\frac{1}{2}H_2O$, as a yellow, non-crystalline crust which was completely soluble in water. The soln. is decomposed by acids with the separation of sulphur. Unlike the pentathionate it is said to give a copious precipitate of sulphur when treated with ammonia. It is more easily decomposed than the pentathionate. The aq. soln. always contains a little sulphur, but the amount does not increase with time ; and sulphur reappears after the liquid has been filtered. E. H. Riesenfeld and G. W. Feld said that the so-called hexathionic acid or hexathionate does not exist, being probably pentathionate containing colloidal sulphur. H. Bassett and R. G. Durrant also consider that the existence of hexathionic acid is improbable—*vide* supra, the constitution of polythionic acids.

E. Weitz and F. Achterberg observed no evidence of the existence of hexathionic acid in Wackenroder's soln., but there were signs of the presence of acids with a larger proportion of sulphur.

A. Kurtenacker and A. Czernotzky observed that in the action of conc. hydrochloric acid on soln. of sodium thiosulphate in the presence of small quantities of sodium arsenate at −10° to −15°, isomorphous mixtures of pentathionate and hexathionate were formed. These decompose rapidly in aq. and dil. acetic acid soln. with the separation of sulphur.

E. Weitz and F. Achterberg prepared potassium hexathionate by the addition of a soln. of a mol of potassium nitrite and about 3 mols potassium thiosulphate to well-cooled hydrochloric acid. The mixture is vigorously shaken until the colour passes through brown and green to yellow, after which the nitrous fumes are removed in a current of air, leaving a soln. having an odour of sulphur dioxide; it is allowed to stand in a freezing mixture until it becomes almost colourless. The precipitated potassium chloride is removed, and the filtrate concentrated under diminished press., whereby potassium hexathionate, mixed with potassium chloride, separates. The chloride is removed by water and the residue washed with alcohol and ether. The mother-liquors from the hexathionate contain considerable quantities of potassium tetrathionate. The production of the latter compound is readily explained either by the intermediate formation of nitrosylthiosulphuric acid or by a simple oxidation of the thiosulphate, but the mode of formation of the hexathionate is obscure. The smallest proportion of nitrite required to prevent the precipitation of sulphur when the soln. is acidified depends on the presence or absence of air and on the concentration of nitrite and thiosulphate in the soln.

E. Weitz and F. Achterberg observed that potassium hexathionate is stable when dry, but it readily decomposes in aq. soln. with the formation of sulphur or a higher polythionate. The addition of acid stabilizes the soln. It crystallizes with difficulty from aq. or feebly acidic soln., most readily from such as contain considerable amounts of mineral acid; from these soln. it can be salted out. Like the pentathionates, it deposits sulphur when treated with alkali; gives yellow and yellowish-white precipitates with mercurous nitrate and mercuric chloride; it does not react with copper sulphate; and gives a brown coloration, passing into a black precipitate, with ammoniacal silver soln. It is more rapidly decomposed than pentathionates by dil. aq. ammonia, tetrathionate being the first product to separate; sodium carbonate soln. behaves similarly. Alkali sulphites rapidly convert hexathionate into trithionate. Potassium hexathionate gives crystalline precipitates with cobaltic and chromic hexamminochlorides and hexamminonitrates, and with cobaltic *trans*-dichlorodiethylenediaminochloride; this behaviour is also shown by the lower polythionates towards the last-mentioned reagent. The anhydrous benzidine salt was prepared. J. R. Partington and A. F. Tipler confirmed the observations of E. Weitz and F. Achterberg on the preparation of the salt. J. A. Christiansen prepared *p-toluoyl hexathionate.*

E. J. Maumené said that *barium hexathionate*, BaS_6O_9, is prepared by mixing three mols of barium thiosulphate with two gram-atoms of iodine. The mixture becomes colourless in 3 or 4 days, and it may then be filtered through cotton-wool, and the crystals washed with alcohol. The salt gives a white precipitate with silver nitrate, which turns black and the liquid at the same time becomes acidic. Colourless, soluble crystals of *sodium hexathionate*, $Na_2S_6O_9.nH_2O$, were also reported. These results have not been confirmed.

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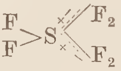
§ 46. Sulphur Fluorides

H. Davy,[1] and J. B. A. Dumas seem to have prepared a *sulphur fluoride* by distillation from mixtures of lead or mercuric fluoride; and, added L. Pfaundler, sulphur does not react with lead fluoride below 140°. According to G. Gore, sulphur reacts with molten silver fluoride, forming silver sulphide and a heavy, colourless vapour of sulphur fluoride which does not condense at 0°; it fumes in air, and has a smell recalling that of sulphur chloride and sulphur dioxide. The composition of these products was not determined. On the other hand, H. Moissan and P. Lebeau prepared **sulphur hexafluoride,** SF_6. They found that sulphur ignites in fluorine gas and burns with a livid flame, forming a gaseous product which consists of two compounds, one of which, though quite insoluble in water, partially dissolves in an aq. soln. of potassium hydroxide. When the fluorine is in excess, the product contains 80–90 per cent. of the insoluble component. Analyses of the insoluble gas show that it is the hexafluoride. The gas was isolated by liquefying the mixture at —80°, and freed from foreign gases by fractional distillation; treated with potash-lye; and dried over fused potassium hydroxide. It is freed from the last traces of nitrogen by liquefaction, and allowing the nitrogen to pass off with the first fraction.

H. Moissan and P. Lebeau found that sulphur hexafluoride is a colourless, odourless, tasteless, incombustible gas. Its **relative density** (air unity) is 5·03—the theoretical value for SF_6 is 5·06. E. B. R. Prideaux represented the electronic structure:



Sulphur hexafluoride was found by H. Moissan and P. Lebeau to solidify at —55° to a white, crystalline mass which melts and boils at slightly higher temp. but E. B. R. Prideaux gave —56° for the **melting point;** —62° for the **boiling point;** and 54° for the **critical temperature.** The coeff. of **thermal expansion** of the liquid is 0·027; the **specific gravity,** 1·91; and the **molecular volume,** 76·5. The **refractivity** μ=1·000783, when the value calculated by the additive law is 1·001116. E. B. R. Prideaux also discussed the relationship between the hexafluorides of sulphur, selenium, and tellurium. H. Moissan and P. Lebeau found that sulphur hexafluoride is a very inert gas resembling nitrogen more than sulphur chloride. M. Berthelot found that it is stable when exposed to the silent electrical discharge. H. Moissan and P. Lebeau found that no change occurs when the gas is heated alone to the softening temp. of hard glass; but at the temp. of the induction spark, it is partially decomposed, but after 2 hrs.' action, 11 per cent. remains unchanged. When sparked in the presence of **hydrogen,** the hexafluoride is completely decomposed with the production of hydrogen sulphide and hydrogen fluoride; these compounds acting on the glass containing vessel form a yellow solid containing sulphur, silica, and hydrofluosilicic acid. A mixture of the hexafluoride and **oxygen,** when strongly sparked, yields a brown, flocculent solid—one part by vol. of oxygen is absorbed, and the total contraction is 2 vols. If the current density is diminished, sulphur oxyfluoride is formed which is less rapidly decomposed by water than is thionyl fluoride. The hexafluoride is very sparingly soluble in **water.** The gas is not affected by **fluorine,** nor by **chlorine, bromine,** or **iodine** at a red-heat. M. Berthelot said that it is not absorbed by bromine. H. Moissan and P. Lebeau said that **hydrogen chloride** has no action on the gas. When the hexafluoride is heated in **sulphur** vapour in a glass vessel, silicon tetrafluoride and sulphur dioxide are formed; if the heating is prolonged, decomposition is complete. It is rapidly attacked by **hydrogen sulphide:** $3H_2S+SF_6=6HF+4S$, and the hydrogen fluoride attacks the glass containing vessel. The gas is decomposed by **selenium,** but the reaction is more complicated than it is with sulphur because a mixture of silicon tetrafluoride, and of sulphur and selenium dioxides, is produced. The gas is not affected by **ammonia**; nor do **phosphorus**, or **arsenic** exert chemical action even at a red-heat. A similar remark applies to the action of **boron, carbon,** and **silicon.** It is rather more soluble in **alcohol** than in water. M. Berthelot said that it is not absorbed by **thiophene.** Sulphur hexafluoride was found to resist the action of **copper** and **silver** at a red-heat; boiling **sodium** rapidly attacks the gas; but **calcium** and **magnesium,** when heated in the gas, are only superficially attacked. The hexafluoride is not affected when heated with **copper oxide,** or **lead chromate**; and it resists the action of **potassium hydroxide**—whether fused, or in alcoholic or aq. soln. M. Berthelot added that it is not absorbed by an acid soln. of **cuprous chloride.**

O. Ruff and K. Thiel attempted to make **sulphur tetrafluoride,** SF_4, by heating nitrogen tetrasulphide with hydrofluoric acid with and without cupric oxide, but obtained instead thionyl fluoride, $N_2S_4+3CuO+20HF=3SOF_2+S$ $4NH_4F(HF).3CuF_2$. Sulphur tetrachloride was not altered when heated with hydrogen fluoride, nor was there any change when titanium tetrafluoride was heated with sulphur tetrachloride; while with stannic fluoride a complex $SCl_4.SnF_4$, or else $SF_4.SnCl_4$, was formed; with arsenic trifluoride, a complex $2AsF_3.SCl_4$ was formed; and negative results were also obtained with antimony trifluoride, and silver fluoride.

M. Centnerszwer and C. Strenk obtained **sulphur monofluoride,** S_2F_2, by heating in vacuo a mixture of a gram of silver fluoride with 4 grms. of sulphur. About 100 c.c. of a gas are evolved. The gas does not condense at ordinary temp. The mol. wt. of the gas calculated from the vapour density and the analysis agree with the formula S_2F_2. The same gas is obtained by heating a mixture of mercurous fluoride and sulphur. The colourless gas has an odour similar to but more objectionable than that of sulphur monochloride. The m.p. is −105·5°; the b.p., −99°; and the sp. gr. at −100°, 1·5. The gas is not stable towards heat, and when introduced into a dry, evacuated flask, it yields a white or yellow deposit, but the decomposition ceases after 12–24 hrs., and the purified gas then gives no deposit when introduced into a second flask, and it does not attack mercury. The impure gas blackens mercury owing to the formation of mercury sulphide. It is therefore supposed that the gas when formed from silver fluoride and sulphur is accompanied by other fluorides relatively difficult to volatilize. The gas deposits sulphur when exposed to air, and likewise also in the presence of moisture. It is absorbed by a soln. of potassium hydroxide.

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§ 47. Sulphur Chlorides

In 1782, A. Hagemann[1] observed that sulphur unites chemically with chlorine, and T. Thomson in 1804 and A. B. Berthollet in 1807 observed that sulphur monochloride, S_2Cl_2, is formed. The composition was afterwards established by H. Davy, and C. F. Bucholz. F. Donny and J. Mareska found that at ordinary temp., and even at −90°, powdered sulphur slowly absorbs chlorine at ordinary temp. with the development of heat, and that the absorption is faster if the sulphur be sublimed in the chlorine gas. The four **sulphur chlorides** have been reported: the tetrachloride,

SCl_4; the dichloride, SCl_2; the tritatetrachloride, S_3Cl_4; and the monochloride, S_2Cl_2; but G. Chevrier, and F. Isambert seem to have considered the first two to be soln. of chlorine in the monochloride; while L. Carius registered only **sulphur dichloride,** SCl_2. M. Trautz said that the main reaction of sulphur and chlorine at a high temp. involves $S_2Cl_2+Cl_2 \rightleftharpoons 2SCl_2$; and that sp. ht. data agree with the assumption that there are formed in the gaseous or liquid state *sulphur hemichloride*, S_2Cl; sulphur tritadichloride, S_3Cl_2; and *sulphur tetritadichloride*, S_4Cl_2.

W. Biltz and E. Meinecke found that sulphur monochloride is soluble in liquid chlorine. According to O. Ruff and G. Fischer, the m.p. curve of mixtures of sulphur with from 51·5 to 92·5 per cent. of chlorine shows a maximum at —80°, and one at —30·5° corresponding respectively with the monochloride and the tetrachloride. There is an indication of a maximum corresponding with *sulphur henachloride*, SCl_{11}, but this has not been confirmed. There is a eutectic melting at —113°, and when it solidifies at —113°, there is an abrupt rise of temp. to —101·3°. There is no evidence of the existence of sulphur dichloride on the m.p. curve. O. Ruff and G. Fischer's data, in atomic percentages, are:

S .	7·7	9·1	12·7	21·6	31·6	35·7	42·6	48·8	51·1
M.p.	38°	39°	−34°	−30·5°	−56°	−69°	−113°	−83°	−81·5

To these A. H. W. Aten added for 20·0, 33·7, 45·3, and 48·6 at. per cent. of sulphur, respectively —30°, —65°, —90°, and —82°; and for the system S_2Cl_2–S_8, with molar percentages of S_8:

S .	4·3	6·0	9·9	28·5	55·4	81·8	81·8	88·4	100°
M.p.	−16°	0°	17·9°	55·2°	77·7°	95·6°	86·0°	10·32°	118·8°
	Rhombic sulphur.						Monoclinic sulphur.		

T. M. Lowry and co-workers measured the f.p. curve of the system: S–Cl by heating the mixture to 100° in a sealed tube to make sure that equilibrium was really attained. Similar results were obtained using iodine as a catalyst. The portion of the curve shown in Fig. 136, indicates that not only is sulphur monochloride formed, but also sulphur dichloride, as well as **sulphur tritatetrachloride,** S_3Cl_4. A mixture having the composition of the dichloride, deposits crystals of the tetrachloride on cooling. The equilibrium between the sulphur chloride in middle regions of concentrations is probably dominated by two simultaneous reactions: $2SCl_2 \rightleftharpoons S_2Cl_2+Cl_2$, and $3SCl_2 \rightleftharpoons S_2Cl_2+SCl_4$; the combination of the monochloride and chlorine is slow at atm. temp. and consequently also the first dissociation is slow. The second reaction is probably a fast one since the reaction $SCl_2+Cl_2 \rightleftharpoons SCl_4$ is fast even at —75°. H. Acker obtained evidence of the formation of a *polythiochloride*, S_4Cl_2 or S_3Cl_2. According to M. Trautz, the change in colour, from yellow to red, which occurs when sulphur is passed into liquid sulphur mono-

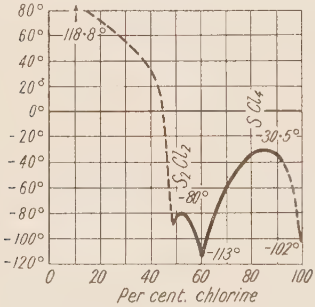


FIG. 136.—Melting-point Curve of Sulphur and Chlorine.

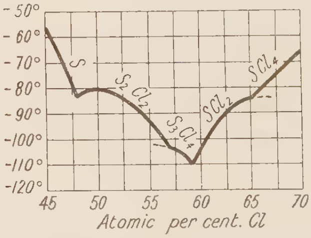


FIG. 137.—Freezing-point Curve of the System: S–Cl after heating to 100°.

chloride, is influenced by several factors—*e.g.* unless the liquid is seeded with sulphur dichloride, SCl_2, the colour change does not occur until the lapse of 3 or 4 hrs. The absorption of chlorine is represented by the scheme: $S_2Cl_2+Cl_2=2SCl_2$. The reaction is very slow unless the sulphur monochloride happens to be in the active state, or when a large proportion of sulphur dichloride, sulphur tetrachloride, stannic chloride, or iodine has been added. The reaction occurs in stages: $S_2Cl_2+Cl_2\rightleftharpoons S_2Cl_4$ (fast); and $S_2Cl_4=2SCl_2$ (slow). There are also the reactions: $SCl_2+Cl_2\rightleftharpoons SCl_4$ (very fast), and $S_2Cl_2+SCl_4=SCl_2+S_2Cl_4$ (measurable but fast). Sulphur dissolved in sulphur monochloride reacts with chlorine in accord with a reaction of the first order. M. Trautz measured the partition coeff. of chlorine in the gas phase, and dissolved in the sulphur monochloride—both fresh and old. T. M. Lowry and G. Jessop observed that the red component is sulphur dichloride, and this can be estimated from the absorption of light of wave-length 5200 A. or 5400 A. to which the monochloride and chlorine are transparent. Sulphur tetrachloride is not formed in appreciable quantities in liquid chlorides of sulphur which behave as ternary equilibrium mixtures, to which the law of mass action can be applied in accord with: $2SCl_2\rightleftharpoons S_2Cl_2+Cl_2$.

H. W. B. Roozeboom's and A. H. W. Aten's observations on the b.p. curves of mixtures of sulphur and chlorine at 740 mm. press. are shown in Fig. 138, where the lower curve represents the composition of the liquid at the b.p., and the upper curve, the composition of the vapour. The dotted curves only partially realized refer to mixtures of sulphur monochloride and chlorine. The following is a selection of the data, where concentrations are expressed in atomic per cent.:

B.p. .	−25·0°	−16·4°	12·0	32·0°	51·4°	105°	150·4°	212°	320°
Liquid .	11·4	17·1	29·2	32·0	36·0	48·0	66·4	90·5	96·1
Vapour .	—	0·8	5·3	18·0	25·6	40·0	49·4	49·9	55·5

A. H. W. Aten said that the character of the variation of vap. press. with composition shows that at 0° the compound SCl_2 is present in the mixtures and is partly associated. The variation of b.p. with composition for mixtures of disulphur dichloride and chlorine confirms the existence of the compound SCl_2, and indicates also the existence of the compound SCl_4. It appears further from these b.p. curves that sulphur monochloride is dissociated to a small extent at its b.p. It has been possible to determine the b.p. of mixtures containing only the molecules S_2Cl_2 and Cl_2, for freshly-prepared mixtures of these substances are yellow in colour, whilst mixtures which have stood for some time are red, have a different b.p., and may be shown to contain at least one compound (SCl_2). It thus appears that the formation of the compound SCl_2 from $S_2Cl_2+Cl_2$ takes place more or less slowly. A. Michaelis made a few observations on this subject; and O. Ruff and G. Fischer determined the composition of liquid and vapour between −10° and 0°, and concluded that between these temp., the so-called sulphur dichloride is a mixture of several substances and not a chemical individual.

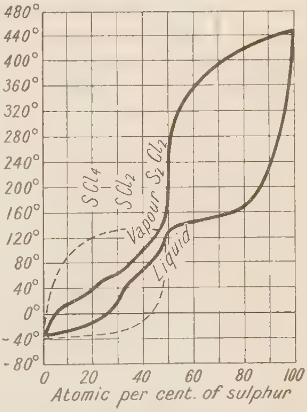


Fig. 138.—The Composition of Binary Mixtures of Sulphur and Chlorine—Liquid and Vapour — at the Boiling Point.

According to J. J. Berzelius, H. Rose, and R. F. Marchand, **sulphur monochloride,** S_2Cl_2, is produced by the action of chlorine on sulphur, or on a metal sulphide as indicated in the patent process of the Consortium fur elektrochemische Industrie; or of sulphur on a metal chloride—*e.g.* stannous or mercuric chloride. E. Legeler used iodine, iron, or iron chloride as catalyst. The mode of preparation by the action of chlorine on heated sulphur is as follows:

A 250 c.c. tabulated retort is fitted with a condenser, and a suction flask as receiver. 100 grms. of flowers of sulphur are introduced into the retort, which is then connected with an inlet tube for chlorine which is washed with water, and dried by conc. sulphuric acid. The retort is heated by an air-bath between 200°–250°. As the rapid current of chlorine passes through the system, sulphur chloride is formed and distilled into the receiver. The black residue which remains in the retort is due to impurities in the sulphur. The crude product is mixed with 10–15 grms. of sulphur, and then distilled from a fractionating flask provided with a condenser and receiver; that which collects below 134° can be poured back into the distilling flask and more sulphur added. The fraction boiling between 137° and 138° is collected. Towards the end of the operation the temp. may rise a few degrees above this temp. owing to the superheating of the vapour. The excess of sulphur remains in the distillation flask. The preparation can be further purified by another fractionation. It distils at 41° under a press. of 28 mm. Moisture present in the chlorine may form some trioxytetrachloride, $S_2O_3Cl_4$ (*q.v.*).

E. Terlinck said that the formation of sulphur monochloride when chlorine is passed into molten sulphur is accompanied by the production of considerable amounts of higher sulphur chloride, which dissolve in the monochloride, but if the mixed chlorides are heated for some time under a reflux condenser the vapour ultimately assumes the b.p. of sulphur monochloride. The reaction, therefore, to produce only the monochloride is dependent largely on the temp., and is best carried out in a soln. of sulphur in boiling sulphur chloride.

An iron vessel is fitted with an iron reflux column and a condenser, and is charged with sulphur and sulphur chloride, which is then heated to boiling. Dry chlorine is passed rapidly into the soln., and when the sulphur is almost completely used up about two-thirds of the mixture is distilled and the resulting sulphur monochloride collected, more sulphur then being added and the process repeated. The distillation may proceed while chlorine is still being absorbed, and the amount of chlorine added may be ascertained by the decrease in weight of the chlorine cylinder or by passing the gas through a gas-meter.

W. J. Pope and fellow-workers prepared sulphur monochloride by distilling the commercial monochloride with the addition of sulphur and about one per cent. by weight of highly absorbent charcoal. The fraction which distils at approximately 137° is redistilled with sulphur and absorbent charcoal under 11 mm. press.—golden-yellow sulphur monochloride distils over at 40°. In C. E. Acker's manufacturing process, sulphur is dissolved in sulphur chloride and the soln. is transferred to a reaction chamber in which it is sprayed through an atm. containing chlorine. The product is then returned to the dissolving chamber, where it is made to take up more sulphur and the cycle of operations is repeated. R. E. Gegenheimer and M. Mauran treated with chlorine a deep bath of sulphur chloride in contact with molten sulphur, and so regulated the temp. that only the monochloride distils over. R. Weber observed that sulphur monochloride is formed by the action of chlorine—best in the presence of a trace of iodine—on carbon disulphide: $CS_2+3Cl_2=CCl_4+S_2Cl_2$; the by-product is then carbon tetrachloride; while sulphur monochloride is a by-product in the preparation of carbon tetrachloride from carbon disulphide and chlorine as described by B. M. Margosches. H. Goldschmidt observed that the monochloride is formed by the action of phosphorus pentachloride on sulphur: $S_2+PCl_5=PCl_3+S_2Cl_2$; and E. Baudrimont, and G. Chevrier obtained it by the action of phosphorus pentachloride on metal sulphides; by heating thiophosphoryl chloride in a sealed tube to redness, or by the action of chlorine on thiophosphoryl chloride; L. Carius, by heating thionyl chloride with phosphorus sulphide; H. Prinz, by heating thionyl chloride with sulphur to 180°; and A. Besson, by the action of hydrogen sulphide on sulphuryl chloride. The New Jersey Testing Laboratories purified crude sulphur chloride by agitating it with small amounts of finely-divided adsorbent substances, such as kieselguhr, china clay, calcium carbonate, or the like, whereupon foreign metallic and organic impurities are removed and a clear liquid possessing a light lemon colour results. It is preferable to employ substances, such as calcium carbonate, which simultaneously remove any free acid present. The process may also be applied by filtering the crude liquid through a bed of the adsorbent material. Any of the chlorides of sulphur may be treated, as the same type of metallic residues and foreign colouring matters occur in each.

Sulphur monochloride appears as a yellowish-red, heavy liquid, which fumes in air; it has a disagreeable, suffocating odour which has been likened to that of sea-weed; its vapour excites tears; it attacks the mucous membrane; and its taste is said to be sour, hot, and bitter. When rectified by distillation in vacuo, it has a pure yellow colour. The freedom of the liquid from any tinge of red is taken to indicate that the monochloride is not contaminated with the higher sulphur chlorides. On heating sulphur monochloride at 60° its colour darkens considerably, and the red tint acquired deepens as the temp. is raised to the b.p.; on cooling, the colour becomes rather lighter, but the pure yellow colour of the original preparation is not regained even after many weeks' standing. When this feebly red-tinted material is treated with absorbent charcoal the colour immediately reverts to the original pure yellow. Sulphur monochloride thus undergoes slight dissociation into sulphur dichloride and sulphur when heated, and, in the absence of a catalyst such as charcoal, the establishment of the equilibrium proceeds very slowly. Analyses were made by J. B. A. Dumas, R. F. Marchand, J. Dalziel and T. E. Thorpe, H. Rose, and C. F. Bucholz, and these are in agreement with the empirical formula SCl. The relative **vapour density** found by J. B. A. Dumas is 4·70, and by R. F. Marchand, 4·77. These numbers are in agreement with the formula S_2Cl_2. G. Oddo and E. Serra found that the **molecular weight,** calculated from the effect of the monochloride on boiling carbon tetrachloride, and boiling benzene, is 169 to 193 when the value for S_2Cl_2 is 135. This seems to indicate polymerization, but the result is attributed to the volatility of the dissolved substance at the temp. of the boiling soln.; but when a due allowance was made for this, a little polymerization was still in evidence, although G. L. Ciamician's correction made the data agree with the normal mol. wt. G. Oddo and M. Tealdi obtained a normal value for the effect of the monochloride on the f.p. of phosphoryl chloride; and G. Bruni and M. Amadori, on the f.p. of bromoform. E. Beckmann, and T. Klopfer found that the mol. wt. is normal when calculated from the effect of the monochloride both on the b.p. and f.p. of chloride or bromine; and E. Beckmann and F. Junker obtained normal values for the mol. wt. from its effect on the b.p. of carbonyl chloride, ethyl chloride, and sulphur dioxide. The constitutional formula may be Cl.S.S.Cl, or, according to A. Michaelis and O. Schifferdecker, H. L. Olin, L. Carius, and T. E. Thorpe, $S{=}S{=}Cl_2$, analogous with thionyl chloride, $O{=}S{=}Cl_2$, and it has accordingly been called *sulphothionyl chloride.* B. Holmberg said that its action on mercaptan favours the formula Cl—S—S—Cl. According to G. Bruni and M. Amadori, just as a series of persulphides is produced by the introduction of sulphur to hydrogen sulphide, H—S—H, $H{-}S_2{-}H$, and $H{-}S_n{-}H$, so may the corresponding sulphur chlorides, sulphur dichloride, Cl—S—Cl, sulphur monochloride, $Cl{-}S_2{-}Cl$, and Cl—Sn—Cl, be possible. M. M. Richter has indicated the existence of organic derivatives of *sulphur tritadichloride*, S_3Cl_2, for he found that sulphur monochloride, S_2Cl_2, acts under some conditions as if it were a mixture of sulphur chloride, SCl_2, and trisulphur dichloride, S_3Cl_2—forming, for instance, the compound sulphides when it reacts with *p*-chlorophenol. The yield of the trisulphide is augmented if sulphur is also employed. G. Bruni and M. Amadori found that a mixture of sulphur monochloride and sulphur depresses the f.p. of bromoform by an amount less than the sum of the depressions produced by the two solutes taken separately. It is assumed that such a soln. contains polythionic chlorides in equilibrium with their components; the divergence of the actual from the calculated depression indicating approximately the formula of the complex chloride. In bromoform soln., the highest such complex compound definitely known to be present is the tetrathionic chloride, that is, **sulphur tetritadichloride,** S_4Cl_2, but chlorides richer in sulphur probably exist in soln. of sulphur in the monochloride. The presence of these polythionic chlorides is due to the formation of polythio-derivatives by the action, substitutive in character, of sulphur monochloride on organic substances. Again, in the cold vulcanization of caoutchouc by means of sulphur monochloride, products may be formed containing sulphur in excess of the ratio S : Cl. O. Ruff and H. Golla found that a sat. soln. of sulphur in sulphur monochloride corresponds closely with the formula S_4Cl_2. Observations on the b.p. of these soln. agree with the assumption that sulphur tritadichloride, S_3Cl_2, and tetritadichloride, S_4Cl_2, are present as well as S_8-molecules. The dissolution of the sulphur is attended by the reactions: (i) $S_8+8S_2Cl_2\rightleftharpoons 8S_3Cl_2$, for which K, in $[S_3Cl_2]^8=K_1[S_8][S_2Cl_2]^8$, is $9{\cdot}758\times10^{-7}$; and (ii) $S_8+4S_2Cl_2=4S_4Cl_2$, for which K_2, in $[S_4Cl_2]^4=K_2[S_8][S_2Cl_2]^4$, is $4{\cdot}533\times10^{-3}$; and (iii) $S_2Cl_2+S_4Cl_2\rightleftharpoons 2S_3Cl_2$, from which K_3, in $[S_3Cl_2]^2=K_3[S_2Cl_2][S_4Cl_2,]$ can be calculated. In conc. soln., the sulphur is nearly all present as S_4Cl_2 and S_8 molecules.

J. B. A. Dumas found the **specific gravity** of the monochloride to be 1·687; R. F. Marchand, 1·686; A. Leboucher gave 1·737 at −18°, and 1·582 at 77°; T. E. Thorpe, 1·70941 at 0°, or 1·69802 at 7·58°; C. A. Fawsitt, 1·7044 at 0°, and 1·6822 at 15·5°; H. Kopp, 1·7055 at 0° and 1·6802 at 16·7°; H. V. Regnault, 1·6970 at 5°–10°; 1·6882 at 10°–15°; and 1·6793 at 15°–20°; A. E. Kretoff, 1·6824 at 20°/20°; and A. Haagen, 1·6828 at 20°. F. M. Jaeger's values are indicated below. E. H. Harvey and H. A. Schuette gave 1·67328 at 25°/4°; T. E. Thorpe, 1·49201 for the sp. gr. at the b.p.; and W. Ramsay, 1·4848. For the **molecular volume,** H. Kopp gave 91·6; W. Ramsay, 90·9; T. E. Thorpe, 90·28. O. Loth studied the subject; and S. Sugden, and E. Rabinowitsch, the mol. vol. A. H. W. Aten found the mol. contraction, δv c.c., of mixtures of chlorine with p per cent. of sulphur monochloride:

S_2Cl_2	11·2	28·7	35·6	44·7	54·6	76·6 mol per cent.
δv	0·25	0·35	0·60	0·67	0·59	0·30 c.c.

thus showing a maximum when the proportion of chlorine corresponds with $S_2Cl_2+Cl_2$, or with SCl_2. I. I. Saslowsky studied the contraction which occurs when the compound is formed from its elements. M. Trautz gave for the sp. gr. of soln. of sulphur in grams per 100 grms. of sulphur monochloride.

Sulphur		0	2	4·2	10	20	25	35
Sp. gr.	0°	1·7090	1·7140	1·7168	1·7274	1·7485	1·7530	1·7670
	10°	1·6950	1·6989	1·7079	1·7137	1·7340	1·7410	1·7540
	20°	1·6790	1·6833	1·6885	1·6978	1·7204	1·7280	1·7409
	40°	1·6480	1·6540	1·6560	1·6700	1·6920	1·7020	1·7170
Mol. vol. (fresh)	0°	0·585	0·583	0·582	0·579	0·572	0·570	0·566
	10°	0·590	0·589	0·587	0·583	0·577	0·574	0·570
	20°	0·596	0·594	0·592	0·589	0·581	0·579	0·574
	40°	0·607	0·604	0·604	0·599	0·591	0·587	0·582
Mol. vol. (aged)	0°	0·585	0·583	0·582	0·578	0·572	0·570	0·566
	10°	0·590	0·589	0·586	0·583	0·577	0·574	0·570
	20°	0·596	0·593	0·592	0·588	0·581	0·579	0·574
	40°	0·607	0·685	0·603	0·598	0·591	0·588	0·584

The sp. gr. of soln. of chlorine in sulphur monochloride, expressed in percentages, were:

Chlorine		0	4·32	7·3888	11·24
Sp. gr.	0°	1·7085	1·7086	1·7066	1·6875
	10°	1·6946	1·6938	1·6932	1·6676
	20°	1·6787	1·6783	1·6776	1·6512
	40°	1·6489	1·6479	1·6466	1·6156

F. M. Jaeger's values for the sp. gr. of the liquid, D, referred to water at 4°, the **surface tension,** σ, in dynes per cm., the **specific cohesion,** A^2 per sq. mm.: and the mol. **surface energy,** $k=d\{\sigma(Mv)^{\frac{2}{3}}\}/dt$, in ergs per sq. cm., are:

D	0°	25·4°	50·1°	75°	90·5°	105·4°	121°
σ_2	45·4	41·8	38·0	34·6	32·9	31·2	29·4
A	5·42	—	4·75	4·43	—	4·12	3·95
k	836·1	781·7	721·9	668·3	641·7	614·8	585·7

The temp. coeff. of k is about 2·24 at 50°, and thereafter falls to about 1·79 ergs per degree. W. Ramsay and J. Shields gave 42·29, 38·00, and 33·81 dynes per cm. for the surface tension respectively at 15·5°, 46·3°, and 78·3°; and for the mol. surface energy, respectively 787·2, 719·6, and 653·6 ergs. W. D. Harkins, and W. Herz studied some relations of the surface tension. E. H. Harvey and H. A. Schuette found the surface tension to be 40·78 dynes per cm. at 22°; and the relative **viscosity,** water unity, 1·908 at 18°. M. Trautz gave for the viscosity coeff., η, of soln. of sulphur in grams per 100 grms. of sulphur monochloride:

Sulphur		0	2	4·2	10	20	25	35
η (fresh)	0°	1289	1319	1396	1629	2109	2371	3014
	10°	1098	1159	1218	1397	1806	2025	2457
	20°	1029	1047	1098	1244	1587	1751	2123
	40°	901	907	972	1065	1340	1514	1795
η (aged)	0°	1289	1282	1372	1603	2106	2370	3006
	10°	1142	1135	1218	1378	1791	2001	2453
	20°	1029	1039	1082	1223	1579	1742	2116
	40°	906	908	970	1060	1335	1512	1784

The subject was studied by O. Loth. A. Leboucher gave 0·001031 for the coeff. of **thermal expansion** (cubic) between −18° and 77°. H. Kopp found that the thermal expansion corresponded with unit vol. changing to $v=1+0\cdot0_3 9591\theta-0\cdot0_7 381\theta^2+0\cdot0_8 73186\theta^3$, at $\theta°$; while T. E. Thorpe gave $v=1+0\cdot0_3 934250\theta+0\cdot0_6 41082\theta^2+0\cdot0_8 40769\theta^3$. M. Trautz gave for the coefficient of thermal expansion, α, of soln. of sulphur in grams per 100 grms. of sulphur monochloride:

Sulphur		0	2	4·2	10	20	25	25
$\alpha \times 10^4$ (fresh)	0°	8	9	8	8	8	7	7
	10°	9	9	9	9	8	7	8
	20°	9	9	10	8	8	8	7
$\alpha \times 10^4$ (aged)	0°	8	9	7	8	8	7	6
	10°	9	8	10	9	8	7	7
	20°	9	10	10	9	8	8	9

H. V. Regnault gave 0·2024 for the **specific heat** between 10° and 15°; J. Ogier gave 0·220 between 12° and 70°; and M. Trautz, 0·22 at 22°; and for soln. of sulphur and chlorine in the monochloride:

Sulphur	42·64	44·89	47·20	49·33	51·29
Chlorine	57·36	55·11	52·80	50·67	58·71
Sp. ht.	0·208	0·219	0·219	0·226	0·245

at temp. between 21° and 25°. Observations on the **melting point** of mixtures of chlorine and sulphur are summarized in Figs. 135 and 136. O Ruff and G. Fischer gave —80° for the m.p. of sulphur monochloride. Observations on the **boiling point** of mixtures of chlorine and sulphur are summarized in Fig. 136. G. Chevrier gave 136° for the b.p. at 758 mm.; C. A. Fawsitt, 136°–137° at 755 mm.; H. Hübner and A. Guéroult, 137°; A. Haagen, 137·7° at 761·4 mm.; J. B. A. Dumas, W. Ramsay, F. M. Jaeger, 138° at 760 mm.; E. H. Harvey and H. A. Schuette, 138°; T. E. Thorpe, 138·12° at 760 mm.; L. Carius, 138°–139° at 760 mm.; and H. Kopp, 140°. The best representative value is 138°. As indicated above, A. H. W. Aten found that sulphur monochloride is slightly dissociated at its b.p. N. de Kolossowsky calculated values from 5·02 to 6·79 for the **ebullioscopic constant.** W. R. Orndoff and G. L. Terrasse calculated the mol. elevation of the b.p. to be 52·8, and E. H. Harvey and H. A. Schuette, 52·9. The last-named found the **vapour pressure,** p mm., to be:

	0°	10°	20°	40°	59°	80°	100°	120°	138°
p	3·7	6·4	10·7	28·0	60·0	135·0	257·0	469·7	760·0

The results can be represented by $\log_{11} p=7\cdot4550-1880.1T^{-1}$. H. Acker obtained:

	37·65°	62·22°	92·98°	103·7°	123·2°	132·5°	136·2°
p	17·1	58·6	192·1	283·3	495·0	651·7	757·3

A. W. Rick, and M. Trautz gave for the vap. press., *p* mm., of sulphur monochloride :

	37·65°	45·08°	59·00°	70·54°	80·68°	89·65°	100·56°	114·9°	136·4°
p. .	17·1	24·8	49·7	84·3	127·9	176·5	254·5	398·1	757·5

and he represented the results by $\log p = -Q_0/457T + 1\cdot75 \log T + \text{constant}$, where $Q_0 = 815$ Cals. The vap. press. of soln. of sulphur in the monochloride :

	61·1°	72·6°	81·0°	93·9°	104·5°	130·8°	132·9°
p . . .	57·4	91·6	137·2	212·4	311·9	633·9	647·2

The soln. has approximately 57·80 at. per cent. of sulphur. The **heat of vaporization** is 63·9 cals. per gram. J. Ogier gave 49·4 cals. per gram. H. Acker calculated 8500 cals. for the mol. heat of vaporization. N. de Kolossowky studied the relation between the thermal expansion and the heat of vaporization. J. Thomsen gave for the **heat of formation** $(S_{2\text{solid}}, Cl_{2\text{gas}}) = 14\cdot25$ Cals. for the liquid monochloride. J. C. Thomlinson found that the calculated value, 14·933 Cals., agrees best with the assumption that the contained sulphur is bivalent : Cl—S—S—Cl. J. Ogier gave 17·6 Cals., and for the gaseous monochloride, 11·0 Cals. M. Trautz found with rhombic sulphur, $(2S, Cl_2) = S_2Cl_{2\text{liquid}} + 14\cdot5$ Cals. ; the heat of dissolution of chlorine in sulphur monochloride is $S_2Cl_{2\text{liquid}} + Cl_{2\text{gas}} = 2SCl_{2\text{soln.}} + 9\cdot8$ Cals., and $S_2Cl_2 + 3Cl_2 = 2SCl_{4\text{soln.}} + 12$ to 14 Cals. M. Trautz studied the **absorption spectrum** of soln. of sulphur monochloride in carbon tetrachloride, chloroform, ethylene dichloride, and benzene. T. M. Lowry and G. Jessop found that sulphur monochloride is transparent to light of wave-length 5200 A. and 5400 A. ; it has a strong maximum absorption in the ultra-violet, log ϵ being 3·8 at 2660 A., but it cannot be estimated photometrically on account of the absorption of ultra-violet light by the dichloride. H. Becquerel gave 0·984 for the **magnetic rotary power** for sodium light, and for the **index of refraction,** 1·6460 ; T. Costa gave for the *D*- and *C*- lines respectively 1·666 and 1·657 ; and F. F. Martens, for the *G*-, *F*-, and Tl-lines, respectively 1·707, 1·688, and 1·677. P. Walden found sulphur monochloride to be an **ionizing solvent.** H. Schlundt gave 4·8 for the **dielectric constant** at 22°.

A. Leboucher found that **hydrogen** has no action on sulphur monochloride at ordinary temp. A. Besson and L. Fournier observed that on submitting sulphur monochloride to fractionation under atm. press., partial decomposition occurred with production of sulphur dichloride and sulphur. The monochloride is completely reduced by hydrogen under the influence of the silent electric discharge. L. Carius found that when the vapour of sulphur monochloride mixed with **air,** or **oxygen,** is passed through a red-hot tube, the gas burns with a blue flame, forming sulphur di- and tri-oxides and chlorine, but not thionyl chloride. M. Martens said that sulphur monochloride reddens blue litmus, but H. Davy found that this is not the case if the litmus paper be dry. T. Thomson observed that the liquid sinks in **water,** and is slowly hydrolyzed into hydrochloric and thiosulphuric acids and sulphur ; the thiosulphuric acid also decomposes into sulphurous acid and sulphur so that the initial and final products are $2S_2Cl_2 + 3H_2O = 4HCl + H_2SO_3 + 3S$. C. F. Bucholz, and H. Rose said that a little sulphuric acid is formed even if the monochloride contains an excess of sulphur ; and M. J. Fordos and A. Gélis observed that a little pentathionic acid is formed. H. Rose added that 10 days after mixing the monochloride with water some thiosulphuric acid can be detected in the soln., and that about three-fourths of the total sulphur separates as elemental sulphur. L. Carius, and H. L. Olin assumed that the first stage of the hydrolysis furnishes sulphur dioxide and hydrogen sulphide : $S_2Cl_2 + 2H_2O = H_2S + SO_2 + 2HCl$, which then interact to form thiosulphuric acid, etc. This equation, said H. Debus, is entirely hypothetical ; it is not supported by experiments ; and it is advanced by L. Carius as an argument in favour of his view of the constituent of the sulphur chlorides. Sulphur monochloride dissolves in an aq. soln. of sulphurous acid without the precipitation of sulphur, but the smallest quantity of hydrogen sulphide, even with a large excess, produces an immediate precipitate of sulphur. The formation of hydrogen sulphide required by L. Carius's equation does not therefore occur. He therefore favoured the former view that water decomposes the monochloride into thiosulphuric acid, sulphur, and hydrochloric acid: $2S_2Cl_2+3H_2O=H_2S_2O_3+4HCl+2S$. B. Neumann and E. Fuchs, however, considered that L. Carius's equation represents the course of the reaction which is followed by a subsequent reaction between the sulphur dioxide and hydrogen sulphide. After complete decomposition by boiling for several hours, the sulphur was found to be present as follows: as separated sulphur, 29·80; colloidal, 35·14; as trithionic acid, 4·84; as tetrathionic acid, 9·09; as pentathionic acid, 18·26; as sulphuric acid, 1·00; as sulphurous acid, 0·31; as hydrogen sulphide, 0·57; total, 99·0 per cent. of the sulphur present. E. Noack said that the end-products of the reaction are the same as in the reaction between sulphurous acid and hydrogen sulphide; a slight difference in the amount of sulphuric acid produced in the absence of air, is attributed to the oxidizing action of a small quantity of a higher sulphur chloride. It is assumed that the first stages of the reaction can be represented by $S_2Cl_2+2H_2O \rightarrow S_2(OH)_2+2HCl$; $S_2(OH)_2 \rightleftharpoons H_2S+SO_2$ and the presence of sulphur dioxide and hydrogen sulphide can be demonstrated. Attempts to prepare the assumed intermediate compound $H_2S_2O_2$, however, by the action of hydrogen sulphide on sulphur dioxide in the absence of water, *e.g.* in alcoholic soln., or by passing hydrogen sulphide into liquid sulphur dioxide, failed. The reaction under such conditions proceeds thus: $2H_2S+SO_2 \rightarrow 2H_2O+3S$. A. Leboucher found that one vol. of sulphur monochloride, sp. gr. 1·737, at −20° absorbs 310 vols. of chlorine.

L. Carius found that well-cooled sulphur monochloride absorbs **chlorine**, forming a dark, reddish-brown liquid which gives off chlorine as soon as it is removed from the freezing mixture. He said that at −6° to −8° the monochloride forms a soln. of 71·67 per cent. total chlorine; at 0·4° to −2·5°, 70 to 70·39 per cent.; at 6° to 6·4°, 69·18 per cent.; and at 20°, 6·78 per cent.—the theoretical value for SCl_4 is 81·61 per cent., and for SCl_2, 68·87 per cent. The behaviour of mixtures of chlorine and sulphur monochloride has been previously discussed. E. Beckmann found that the mol. wt. of the monochloride in liquid chlorine or **bromine** is normal. G. Chevrier found that sulphur monochloride dissolves bromine and **iodine,** and that the soln. boil below 136°. P. Hautefeuille found that **hydriodic acid** reacts with sulphur monochloride at ordinary temp., forming hydrochloric acid, iodine, sulphur iodide, and finally hydrogen sulphide. H. Feigel found that a benzene soln. of sulphur monochloride after a month's action on **mercurous chloride** at ordinary temp., forms a little mercuric chloride; **cuprous chloride** forms a little cupric chloride and sulphur. Sulphur monochloride in the presence of water transforms **cupric chloride** into cupric sulphide, but **lead chloride** under similar conditions suffers no change.

H. Rose, C. F. Bucholz, and A. B. Berthollet observed that sulphur monochloride dissolves a large proportion of **sulphur,** especially when heated; it then forms a syrupy liquid from which, on cooling, sulphur continues to separate for weeks. When saturated at ordinary temp., the soln. has a sp. gr. 1·7, and contains S : Cl=4 : 1. The f.p. and b.p. of the mixtures are indicated in Figs. 135, 136. T. M. Lowry and co-workers gave Fig. 139 for the solubility curve of sulphur in sulphur monochloride—*vide supra.* D. L. Hammick and M. Zuegintzov found the solubility of sulphur in the monochloride to be greater the higher the temp. to which the sulphur has been preheated. It is thought that the solubility curves indicate the formation of a *sulphur tetritadichloride*, S_4Cl_2, and is not due to a change in the inner equilibrium of the dissolved sulphur. Observations were also made by H. Acker. H. Rose found that **hydrogen sulphide** reacts with the monochloride, forming hydrogen chloride and sulphur: $S_2Cl_2+H_2S=3S+2HCl$, while U. Antony

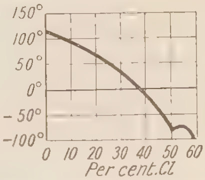


FIG. 139.—Solubility of Sulphur in Sulphur Monochloride.

and G. Magri showed that with the liquid hydrogen sulphide, a red soln. is formed. G. N. Quam and J. A. Wilkinson found the sp. conductivity of a sat. soln. of the monochloride in liquid hydrogen sulphide to be $10 \cdot 340 \times 10^4$ mhos. H. Prinz found that liquid **sulphur dioxide** and sulphur monochloride are completely miscible at ordinary temp., and that they do not act on one another even at 100°. H. Debus's observations on the action of **sulphurous acid** are indicated above. A. Besson and L. Fournier observed that in the absence of an electric discharge sulphur dioxide slowly reacts with the monochloride at 160° to 170°, forming sulphur and sulphuryl chloride. L. Carius said that when heated with **calcium sulphite,** sulphur monochloride furnishes calcium chloride and sulphur dioxide. W. Spring and A. Lecrenier assumed that when **potassium sulphite** acts on the sulphur halides, as many mols. of potassium sulphate are formed for every molar proportion of free halogen, and hence inferred that 6·7 per cent. of the elements of sulphur monochloride are present in the free state, a conclusion not very acceptable. H. Rose found that when cooled below 0°, 5 mols. of **sulphur trioxide** vapour are absorbed per mol. of the monochloride, forming a brown liquid which turns yellow and from which the sulphur trioxide separates in the crystalline form. The resulting complex may be a mixture or *sulphur pentahydrosulphatochloride*, $S_2Cl_2.5SO_3$. If the brown soln. be kept for 24 hrs. in a closed vessel at 0°, it regains its yellow colour provided the sulphur trioxide is not in excess. At temp. below 0°, no sulphur trioxide escapes, but a few degrees above that temp., the gas is vigorously evolved. When the liquid is heated in a retort, it soon boils with the violent evolution of sulphur dioxide, and if the sulphur trioxide be not in excess, the evolution of sulphur dioxide continues as the temp. gradually rises. Between 30° and 40°, sulphur monochloride passes over, then an admixture of pyrosulphuryl chloride, and lastly, at 145°, the pyrosulphuryl chloride alone is evolved. The admixture can be separated by fractional distillation. When sulphur monochloride is treated with a large excess of sulphur trioxide, a thin blue liquid is formed—or a solid if a very great excess of trioxide is used. The mixture becomes colourless when heated, forming a mixture of pyrosulphuryl chloride with an excess of sulphur trioxide. If heated still more, the trioxide passes over first, then an admixture with pyrosulphuryl chloride, and lastly, pyrosulphuryl chloride alone. The blue colour is due to an admixture of sulphur from the monochloride with the trioxide. H. Rose also found that sulphur monochloride, saturated with chlorine, absorbs the vapour of sulphur trioxide until sulphur trioxide begins to crystallize out from the liquid. The liquid slowly crystallizes. The crystals can be kept a long time without change; they fume in air; and explode when thrown on water, forming sulphuric and hydrochloric acids. Analyses agree with $SCl_6.30SO_3$. There is here nothing to show that the product is anything but a mixture of, say, sulphuryl chloride and sulphur trioxide. According to M. Brault and A. B. Poggiale, when a mixture of the vapours of sulphur monochloride and **sulphuric acid** is passed through a red-hot tube, sulphur, sulphur dioxide, hydrogen sulphide, hydrogen chloride, and chlorine are formed. B. Rathke found that the monochloride reacts with **selenium,** forming sulphur and selenium monochloride. F. Krafft and O. Steiner, and R. W. E. MacIvor observed that with an excess of **tellurium** the dichloride is formed; while V. Lenher found that an excess of **tellurium dioxide** forms the dichloride: $TeO_2+S_2Cl_2=TeCl_2+S+SO_2$ and an excess of sulphur monochloride, the tetrachloride: $TeO_2+2S_2Cl_2=TeCl_4+SO_2+3S$.

According to M. Martens, **ammonia** gas reacts with sulphur monochloride, forming sulphur tetramminochloride, $S_2Cl_2.4NH_3$, which, when treated with water, furnishes sulphur and ammonium chloride and thiosulphate. A. K. Macbeth and H. Graham observed that chloroform soln. of sulphur monochloride and ammonia react: $6S_2Cl_2+16NH_3=N_4S_4+12NH_4Cl+8S$—the nitrogen tetrasulphide (*q.v.*) is precipitated by alcohol and the mother-liquor yields nitrogen pentasulphide and hexasulphamide, $S_6(NH_2)$. A. Leboucher observed that **phosphorus** readily dissolves in sulphur monochloride at 12°–15°, and more is dissolved at 25°–30°—at 30°, 100 grms. of the monochloride can dissolve 56·56 grms. of phosphorus. According to H. F. Gaultier de Claubry, phosphorus withdraws chlorine from the monochloride producing a rise of temp. of 40°, and on distilling the liquid, phosphorus trichloride distils over, and sulphur remains. F. Wöhler observed that sulphur monochloride readily dissolves phosphorus with a rise of temp. and forms a pale yellow liquid, which, when cooled, deposits phosphorus contaminated with sulphur, and which, when heated, boils explosively. If pieces of phosphorus be added to warm sulphur monochloride, sulphur is deposited, and phosphorus trichloride and sulphochloride are formed; *au contraire,* if sulphur monochloride be dropped into molten phosphorus, phosphorus trichloride and a yellow sublimate of phosphorus sulphide are produced, and red phosphorus remains behind. G. Chevrier said that if the phosphorus be not in excess, phosphorus sulphochloride and sulphur are formed. E. Baudrimont observed that with phosphorus trichloride the product after fractional distillation furnished crystals, which G. Chevrier said were those of thiophosphoryl chloride: $3PCl_3+S_2Cl_2=PCl_5+2PSCl_3$. A. Michaelis heated phosphorus trichloride and sulphur monochloride in a sealed tube at 160°, and obtained phosphorus pentachloride, and sulphochloride: $S_2Cl_2+3PCl_3=2PSCl_3+PCl_5$. H. Prinz said that **phosphorus pentoxide** does not produce thionyl chloride. A. Leboucher found that at ordinary temp. **arsenic** has no action on sulphur monochloride. F. Wöhler, G. Chevrier, and M. M. P. Muir found that with arsenic, sulphur, and arsenic trichloride are formed: $3S_2Cl_2+2As=2AsCl_3+6S$; and F. Wöhler, and G. Chevrier observed that **antimony** behaves similarly. A. Leboucher said that the energetic nature of the action of liquid sulphur monochloride on powdered antimony is *des plus remarquables.* According to G. Oddo and E. Serra, when **arsenic trioxide** and sulphur monochloride are heated together in a reflux apparatus, they react according to the equation: $As_4O_6+6S_2Cl_2=4AsCl_3+3SO_2+9S$. The reaction is complete in about an hour, and on cooling, nearly all the sulphur formed crystallizes out and the arsenic trichloride can be separated by decantation. An analogous change occurs when **antimony trioxide** is employed. H. Prinz observed that no thionyl chloride is formed when the monochloride acts on arsenic trioxide or antimony trioxide, or on **antimony pentoxide.** G. Oddo and E. Serra observed that **bismuth oxide** behaves like arsenic trioxide. L. Wöhler found that **arsenic disulphide,** or **arsenic trisulphide**, reacts with sulphur monochloride, forming arsenic trichloride and sulphur; similar results were obtained with black **antimony trisulphide.** A. Leboucher, and H. Feigel also observed that the sulphides of arsenic and antimony are energetically attacked at ordinary temp.

A. Leboucher observed no action between **carbon** and sulphur chloride at ordinary temp. or at a red-heat. E. Lorand studied its action on petroleum hydrocarbons. J. Davy observed that sulphur monochloride dissolves **carbonyl chloride**; and A. B. Berthollet, that it readily mixes with **carbon disulphide.** A. Müller and H. Dubois stated that carbon disulphide reacts with sulphur monochloride, particularly in the presence of metals or the metal chlorides—*e.g.* iron, or ferric chloride—according to the equation: $CS_2+2S_2Cl_2=CCl_4+6S$. R. Schneider found that **silver cyanide** reacts with a soln. of sulphur monochloride in carbon disulphide, forming crystals which rapidly decompose into cyanogen sulphide and xanthane. Organic compounds containing oxygen form sulphur, hydrogen chloride, sulphur dioxide, and organic chlorides with traces of sulphides, and unsaturated organic compounds, free from oxygen, yield addition products. Thus, F. Guthrie found that **ethylene** furnishes ethylene disulphochloride, and similarly with **amylene.** The reaction was studied by W. J. Pope and fellow-workers, and by J. B. Conant and co-workers. E. Lorand found that sulphur monochloride reacts vigorously with unsaturated compounds. With normal paraffin hydrocarbons the reaction is slow even upon heating, but side-chain paraffin hydrocarbons react more readily. The reaction is accompanied by the formation of polymerization products and the evolution of hydrogen chloride, and it is suggested that, in the case of paraffins, ethylenic linkings are formed, whilst ethylenic compounds yield two hydrogen atoms to form hydrogen chloride with the formation of a triple linking. P. Friedländer and A. Simon examined the action of sulphur monochloride on **anthracene.** L. Carius represented the first stage of the reaction with **alcohol**: $S_2Cl_2+C_2H_5OH=C_2H_5SH+SOCl_2$; and the second stage: $4C_2H_5SH+3SOCl_2=2C_2H_5Cl+SO(OC_2H_5)_2+6S+4HCl$. J. B. A. Dumas said that the monochloride dissolves in ether when first mixed, but afterwards decomposes with a slight evolution of heat. G. C. Chakravarti, and B. Holmberg found that **mercaptans** react with sulphur monochloride, forming polysulphides. W. Heintz, L. Carius, A. Rössing, and H. F. Morley studied the formation of dichlorhydrin by the action of sulphur monochloride on glycerol, which A. Claus represented by $C_3H_5(OH)_3+2S_2Cl_2=C_3H_5(HO)Cl_2+2HCl+SO_2+3S$; with **glycol,** ethylene chlorhydrin is formed: $2C_2H_4(OH)_2+2S_2Cl_2=2C_2H_4(OH)Cl+2HCl+SO_2+3S$. K. G. Naik and C. S. Patel studied the action of sulphur monochloride on organic acid amides; G. C. Chakravarti, and S. Ishikawa, on thioamides; L. Cassella, aromatic amines; A. Leboucher said that **essential oils**—citron, turpentine, and lavender oils—are energetically attacked by sulphur chloride; there is a rise of temp., white fumes, probably hydrogen chloride, are given off, no sulphur is deposited, but the essence thickens, forming a yellow, gum-like mass. The **fatty oils**—*e.g.* olive oil—are also attacked with a considerable rise of temp., no gas is given off, no sulphur is deposited, and the mass solidifies on cooling. The vulcanizing action of sulphur monochloride on **rubber** was discussed by C. A. Fawsitt; when rubber is dipped into a soln. of sulphur chloride in carbon disulphide, it is vulcanized by a small quantity of sulphur replacing hydrogen—and the evolution of hydrogen can be plainly seen by using a conc. soln. of the chloride. M. M. Richter observed that in some cases sulphur monochloride reacts towards organic compounds as if it were a mixture of *sulphur ditritachloride*, S_3Cl_2, and the dichloride: $2S_2Cl_2=SCl_2+S_3Cl_2$. Thus, with *p*-chlorophenol it forms $S(HO.C_6H_3Cl)_2$, and $S_3(HO.C_6H_3Cl)_2$. P. P. Budnikoff and E. A. Shiloff found that 40 per cent. of **silica** is converted to silicon tetrachloride when 40 grms. of sulphur monochloride act on 5 grms. of silica at 1000°.

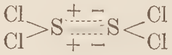
E. Baudrimont found that when heated with the **metals,** sulphur monochloride furnishes chlorides; sodium and magnesium are not so easily attacked; aluminium, tin, and mercury are readily attacked; zinc, iron, nickel, and copper are slowly attacked. F. Wöhler, also, observed that copper, zinc, iron, and nickel are only slowly attacked. E. F. Smith and V. Oberholtzer observed that tungsten forms a complex chlorosulphide, and similarly with molybdenum. N. Domanicky found that the reaction between sulphur monochloride and the metals is favoured by the presence of dry ether, with which the metallic chlorides form complexes, and so enhance the thermal effect of the reaction. Under these conditions, magnesium, zinc, aluminium, tin, iron, mercury, and gold are readily converted into their chlorides or etherates of the latter. On the other hand, the alkali metals, calcium, cadmium, thallium, lead, manganese, cobalt, nickel, copper, silver, and platinum react either not at all or with extreme slowness. The metals which do react either (i) give chlorides which readily form etherates, as is the case with zinc, aluminium, tin, and bismuth, or (ii) give chlorides which are readily fusible and volatile and approximate in their properties to the chloro-anhydrides; in correspondence with the latter, the higher chlorides are mostly formed, for instance, $ZrCl_4$, $FeCl_3$, $HgCl_2$. Univalent metals do not react, and bivalent metals (excepting mercury), if at all, react with far greater difficulty than ter- and quadri-valent metals. It is probable that other metals, giving volatile higher chlorides, such as titanium, germanium, and the like, also react readily with sulphur chloride and ether. P. Nicolardot observed that ferrosilicon, ferrotitanium, and ferrochromium are opened up in this way. G. Chevrier said that boiling sulphur monochloride does not attack sodium; at ordinary temp., potassium is slightly attacked, but when the liquid is warmed, *une violente détonation* is produced; A. C. Vournasos reduced the monochloride in the form of vapour by heated potassium: $S_2Cl_2+4K=2KCl+K_2S_2$. G. Chevrier found that tin is vigorously attacked: $Sn+S_2Cl_2=SnCl_2+2S$; and when agitated with mercury, a vigorous action occurs, and mercuric chloride is formed—if the sulphur monochloride be in excess, mercurous chloride is formed. A. Leboucher found that sodium, potassium, copper, silver, zinc, mercury, tin, and lead form sulphides and chlorides, while platinum is not attacked by boiling sulphur monochloride. According to E. H. Harvey, cobalt and chromium were not affected by sulphur monochloride; the change with nickel, cadmium, lead, and silver was small; but aluminium, copper, arsenic, antimony, and manganese were badly attacked at room. temp. after a year's exposure. A. Leboucher observed no action on the **metal oxides** at ordinary temp.; with many **metal sulphides** there is no perceptible action at ordinary temp., but sulphides of iron and lead are feebly attacked. H. Feigel found that a boiling benzene soln. of sulphur monochloride slowly reacts with zinc sulphide, forming a complex compound of zinc chloride and a thiophenyl-derivative; similar results were obtained with bismuth, lead, and calcium sulphides; silver sulphide forms some silver chloride and sulphur; mercury sulphide forms a sulphochloride, $Hg(SCl)_2$; and stannic sulphide forms the chloride.

According to O. Ruff and H. Golla, aluminium chloride forms with sulphur monochloride the complex **aluminium tetrasulphoheptachloride,** $AlCl_3.2S_2Cl_2$; when heated, **aluminium sulphopentachloride,** $AlCl_3.SCl_2$, is formed; when the original mixture contains free sulphur in the correct proportions, and is heated in a sealed tube, **aluminium hexasulphoheptachloride,** $AlCl_3.2S_3Cl_2$, and **aluminium octosulphoheptachloride,** $AlCl_3.2S_4Cl_2$, are formed, and when the latter is extracted with carbon disulphide, **aluminium tetrasulphotrichloride,** $AlCl_3.2S_2$, is formed, and a prolonged extraction leaves **aluminium disulphotrichloride,** $AlCl_3.S_2$. If aluminium is heated with sulphur monochloride, **aluminium trisulphotrichloride,** $AlCl_3.S_3$, is formed. According to G. Oddo and U. Giachery, the reaction, $2HgO+2S_2Cl_2=2HgCl_2+SO_2+3S$, occurring when mercuric oxide is added gradually to sulphur monochloride, proceeds with greater rapidity and is accompanied by the development of a large amount of heat. The yield of mercuric chloride is almost theoretical. The vapour of sulphur monochloride passed over many heated and metal oxides or **minerals** "opens" them up for analysis so that they are accessible to the usual solvents—*e.g.* R. D. Hall, E. F. Smith, and H. B. Hicks opened up the oxides of columbium, tantalum, titanium, aluminium, and iron; and in consequence the process can be used for preparing the volatile metal chlorides from the oxides; silica and boric oxide are not affected, but chromic oxide is slowly attacked. P. P. Budnikoff and E. A. Shiloff said that at 1000° about 40 per cent. of silica is converted to silicon tetrachloride in an hour. F. Bourion, and E. Defacqz opened up tungsten oxide, zirconium oxide, thorium oxide, and the rare earth oxides; R. W. E. MacIvor, and V. Lenher, the native tellurium minerals; F. Wöhler, and E. Baudrimont, stannous sulphide; and H. Rose, cinnabar. E. F. Smith opened up the oxides of tantalum, columbium, tungsten, tin, zirconium, vanadium, molybdenum, and tungsten as well as the minerals wolframite, scheelite, and columbite. Stibnite, chalcocite, arsenic trisulphide, arsenopyrite, chalcopyrite, cinnabarite, tetrahedrite, marcasite, and pyrites are decomposed at 140°; linnaeite, millerite, gersdorffite, and rammelsbergite are decomposed at 170°; cobaltite, smaltite, and ullmannite are decomposed at 180°; sphalerite, and galenite are decomposed at 250°; and molybdenite at 300°. P. P. Budnikoff and E. A. Shiloff obtained phosphorus trichloride by the action of sulphur monochloride on calcium phosphate at about 1000°.

Sulphur monochloride is used in the vulcanization of rubber; as a chlorinating agent in organic chemistry—*e.g.* in the manufacture of mono- and di-chlorohydrin; as an opening agent for some minerals; and F. von Konek described its use in the preparation of some sulpho-dyes. J. Vosseler suggested its use as an insecticide; and L. de Rigaud, in the extraction of gold.

A. B. Berthollet observed that the chlorination of sulphur occurs in two stages—the first product is orange, the final product is red. J. B. A. Dumas showed that vapour density determinations, and analyses agreed with the respective formulæ

S_2Cl_2 and SCl_2. J. B. A. Dumas, and E. Soubeiran prepared **sulphur dichloride,** SCl_2, by passing dry chlorine in excess for many days over flowers of sulphur, and distilling the liquid between 60° and 70°. The distillate contains some sulphur monochloride, and it is rectified by repeated distillation in a current of chlorine. J. Dalziel and T. E. Thorpe, T. Costa, and H. Hübner and A. Guérout saturated well-cooled sulphur monochloride with chlorine, and expelled the excess of chlorine by the passage of a current of dried carbon dioxide for many hours. L. Carius used a somewhat similar process. E. Beckmann warmed a soln. of sulphur monochloride in liquid chlorine at room temp. and froze from the soln. a product of this composition. According to W. J. Pope and C. T. Heycock, the employment of one per cent. by weight of finely powdered absorbent charcoal as a catalyst greatly facilitates the reaction between chlorine and sulphur monochloride; and similarly when sulphur dichloride is exposed to conditions which lead to its decomposition into chlorine and monochloride, recombination is facilitated by similar means. Analyses made by H. Davy, J. B. A. Dumas, L. Carius, J. Dalziel and T. E. Thorpe, and H. Hübner and A. Guérout agreed with the formula SCl_2. E. Beckmann and F. Junker calculated 147 for mol. wt. from the effect of the dichloride on the b.p. of carbonyl chloride; 147, with ethyl chloride; and 226 with sulphur dioxide. T. Costa, from the effect of the dichloride on the f.p. of acetic acid, gave 103 for the mol. wt., and 97 to 103 from its effect on the f.p. of benzene; whilst E. Beckmann obtained 99 to 103 from its effect on the f.p. of sulphur monochloride. The value calculated for SCl_2 is 103. E. Beckmann said that the mol. wt. deduced from its effect on the b.p. and f.p. of liquid chlorine agrees with the formula CSl_2. G. Oddo also found that the effect on the f.p. of benzene, and the b.p. of benzene and carbon tetrachloride, agree with this formula. It is supposed that some of the dichloride may be practically decomposed in the hot soln.: $2SCl_2 \rightleftharpoons S_2Cl_2 + Cl_2$; $5SCl_2 = 2S_2Cl_2 + SCl_4 + Cl_2$; or $17SCl_2 = 8S_2Cl_2 + SCl_4 + 7Cl_2$. E. B. R. Prideaux represented the electronic structure:



$$\begin{matrix}Cl\\Cl\end{matrix}\!>\!S\overset{+\;-}{\underset{+\;-}{=}}S\!<\!\begin{matrix}Cl\\Cl\end{matrix}$$

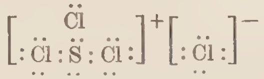
There has been some discussion as to the real existence of sulphur dichloride because L. Carius found that the amount of chlorine contained in the liquid over and above that required by the formula is altogether dependent on the temp., and he assumed that the product analyzed by J. B. A. Dumas, etc., was really a mixture of $S_2Cl_2 + SCl_4$, the latter component had not been at that time isolated. J. Dalziel and T. E. Thorpe, however, added that it is not likely that the results by H. Hübner and A. Guéroult and themselves can be the results of an accidental coincidence. The mol. wt. determinations of the mixture $S_2Cl_2 + Cl_2$ would be reported the same as of $2SCl_2$. H. Rose reported complexes $2AsCl_2.SCl_2$, and F. Guthrie, complexes $C_nH_{2n}SCl_2$; and J. Dalziel and T. E. Thorpe showed that when the product of the action of chlorine on sulphur boiling below 136° is distilled, only a small proportion collects at that temp., but at each redistillation, the liquid becomes lighter in colour, and finally, by a long-continued ebullition, it assumes the bright yellow tint of monochloride and boils at 136°–137°. Hence some compound of chlorine and sulphur is present in addition to the monochloride, and it is only decomposed very slowly on distillation to form the monochloride. As indicated above, A. H. W. Aten, and T. M. Lowry and G. Jessop obtained definite evidence of the existence of the dichloride—*vide* Fig. 136. F. Isambert found that the vap. press. of soln. of chlorine in sulphur monochloride, between 4° and 10°, vary continuously with the amount of chlorine dissolved, and show no evidence of chemical combination. At lower temp. A. Michaelis and O. Schifferdecker obtained evidence of the formation of tetra- and di-chlorides. A soln. of monochloride at −22° absorbs chlorine to form sulphur tetrachloride, and as the temp. rises, the liquid boils, and gives off chlorine. They estimated that at −22° the liquid contained 100 per cent. SCl_4, at 0·7°, 8·87 per cent. SCl_4 and 91·13 per cent. SCl_2; at 20°, no SCl_4, 93·45 per cent. SCl_2, and 6·55 per cent. S_2Cl_2; and at 130°, no SCl_4, or SCl_2, and 100 per cent. S_2Cl_2. T. Costa, H. Hübner and A. Guéroult, E. Beckmann, J. Dalziel and T. E. Thorpe, and A. H. W. Aten consider that the existence of this compound has been proved, while H. Rose, J. Ogier, L. Carius, G. Chevrier, and F. Isambert denied its existence. H. Rose based his objection on the variable composition of the red product; F. Isambert, on the variable vap. press.; and J. Ogier, on the small heat of formation; and it has been said that from the work of O. Ruff and G. Fischer, Fig. 136, *on peut enfin considérer comme définitif.* A. H. W. Aten based his opinion on the fact that the composition of the liquid and vapour phases became almost identical as the composition approached S_2Cl_2, diverged widely on either side; and again approached one another as the composition approached that of the dichloride—provided time is allowed for combination to occur—Fig. 136. He therefore postulated the equilibrium $3SCl_2=S_2Cl_2+SCl_4$ with a temp. coeff. so large that the system deposited SCl_2 at 0° and SCl_4 at −30°. T. M. Lowry and co-workers' f.p. curve—Fig. 136—showed the conditions of existence of sulphur dichloride provided that the elements have sufficient time to interact and assume the equilibrium condition. The dichloride can be recrystallized from light petroleum of b.p. 40° and f.p. −147° by cooling the soln. with liquid air. R. P. Bothamley observed that the reaction can be greatly accelerated by the addition of 0·5 per cent. by weight of antimony pentachloride. The reaction: $S_2Cl_2+Cl_2=2SCl_2$ is completed in about an hour at 19°. There is a period of induction, and the reaction is photochemical, for it proceeds rapidly in direct sunlight. M. Bergmann and I. Bloch said that in the formation of trisulphides of benzoic and arsenic acids by the action of sulphur dichloride on the potassium salts of the thio-acids the sulphur dichloride behaves as a chemical individual. If the dichloride were a mixture of chlorine or of chlorine and sulphur tetrachloride in sulphur monochloride, the action of potassium thiobenzoate should yield a mixture of benzoyl di- and tetra-sulphides which might be mistaken analytically for the trisulphide, but the physical properties are quite different.

Sulphur dichloride is a dark brownish-red liquid which fumes in air, and has a smell more resembling chlorine than is the case with sulphur monochloride; and, as indicated above, it can be obtained in crystals. T. Thomson said that it tastes sour, hot, and bitter. J. B. A. Dumas gave 1·620 for the **specific gravity** of the liquid; A. E. Kretoff, 1·622 at 20°/20°; and T. Costa, 1·64819 at 15·4°. E. Rabinowitsch studied the **molecular volume** —69. J. B. A. Dumas said that the dichloride evaporates without decomposition, but R. F. Marchand observed that when sulphur dichloride is heated, it behaves like a mixture of chlorine and sulphur monochloride, giving off chlorine. L. Carius, and R. F. Marchand did not obtain a constant boiling product between 78° and 139°, but at the latter temp. sulphur monochloride distilled over. G. Chevrier observed similar results under a reduced press. R. F. Marchand said that sulphur dichloride at first boils at 50°, and gives off nearly pure chlorine, the b.p. then rises to 64° when the composition of the liquid approximates SCl_2. J. B. A. Dumas found the **vapour density** to be 3·7 corresponding with 3·56, the value for a mixture of equal vols. of chlorine and sulphur monochloride. W. Spring and A. Lecrenier estimated from its action on potassium sulphite—*vide supra,* sulphur monochloride—that 9·45 per cent. of its elements are in the free state. For the **melting point,** *vide* Figs. 135 and 136. For the action of heat on soln. of chlorine and sulphur monochloride, *vide supra,* and also the observations of F. Isambert, J. Dalziel and T. E. Thorpe, and A. Michaelis and O. Schifferdecker. H. Becquerel gave 0·932 for the **magnetic rotatory power,** and 1·6190 for the **index of refraction** with Na-light; T. Costa, 1·57169 for the H_α-line, and 1·57806 for the Na-line; and F. F. Martens, 1·566 and 1·560 respectively for the *F*- and Tl-lines. For the absorption spectra, *vide supra.*

R. F. Marchand observed that sulphur dichloride evolves chlorine when exposed to sunlight. M. Martens said that the dichloride reddens dry blue litmus paper, but H. Davy contradicted this statement. As shown by A. Leboucher, many of the properties of the supposed sulphur dichloride resemble those of the monochloride. H. Rose found that the dichloride is slowly decomposed by **water,** forming hydrochloric and thiosulphuric acids; some sulphur also separates and a little sulphuric acid is formed. E. Solly found that the dichloride dissolves **iodine,** forming a deep red liquid which does not conduct electricity. P. Jaillard obtained a complex: **iodine sulphoctochloride,** $2ICl_3.SCl_2$. A. Leboucher found that the dichloride dissolves a little more **sulphur** than the monochloride. L. Carius observed that the dichloride acts on **potassium sulphate** at 150°–160°, and on **lead sulphate** at 100°, forming sulphur dioxide, the metal chloride, sulphuryl chloride, and, if the temp. be not too high, sulphur monochloride. J. B. A. Dumas found that with aq. **ammonia,** sulphur, nitrogen, and ammonium chloride are formed. R. Schenck showed that some nitrogen tetrasulphide is formed: $6SCl_2+16NH_3=N_4S_4+2S+12NH_4Cl$. Observations by M. J. Fordos and A. Gélis, O. Ruff and E. Geisel, etc., on this subject are indicated in connection with nitrogen sulphide. E. Soubeiran observed that complexes are formed with ammonia gas—*e.g.* what he called *chlorure de soufre ammoniacal,* or **sulphur diamminodichloride,** $SCl_2.2NH_3$, in brown flecks which are non-volatile—M. Martens said the compound is volatile. It does not redden litmus; it is coloured yellow at 110° and forms ammonium chloride, and what he called *chlorosulfure sulfazotique,* $N_2S_3.SCl_2$, it is decomposed by water; and dissolves in absolute alcohol or ether. He also obtained lemon-yellow flecks of *chlorure de soufre biammoniacal,* or **sulphur tetramminodichloride,** $SCl_2.4NH_3$, which is slightly soluble in anhydrous alcohol or ether and is thereby decomposed. It loses ammonia when heated, forming nitrogen, sulphur, ammonium chloride, and nitrogen sulphide. When treated with cold water nitrogen sulphide separates out and subsequently decomposes. M. J. Fordos and A. Gélis regarded these ammines as mixtures. A. Leboucher said that **phosphorus** dissolves in sulphur dichloride more readily than in the monochloride. T. Thomson found that **nitric acid** converts the dichloride with violent effervescence into hydrochloric and sulphuric acids; the dichloride dissolves **phosphorus,** forming an amber-coloured liquid. H. Rose said that the dichloride forms a complex with **arsenic trichloride.** J. Davy said that the dichloride absorbs **carbonyl chloride.** The dichloride froths up violently when treated with **alcohol;** and J. B. A. Dumas observed a similar result with **ether.** B. Holmberg studied the action of the dichloride on **mercaptan. Organic compounds** containing oxygen were found by F. Guthrie to be more readily attacked than is the case with the monochloride; and with unsaturated organic compounds, addition products are formed. J. B. A. Dumas reported that when a piece of **potassium** is dropped into half a gram of the liquid dichloride, a red light is often produced after about 40 seconds, and an explosion bursts the containing vessel. When the vapour of the dichloride is passed over red-hot **iron** or **copper** turnings the metal chloride and sulphide are produced with the evolution of light and heat.

A. Michaelis and O. Schifferdecker prepared what they regarded as **sulphur tetrachloride,** SCl_4, by saturating sulphur monochloride with sulphur at −20° to −22°; the analysis of the product agreed with the formula. O. Ruff obtained a similar product by mixing the required quantities of sulphur monochloride and liquid chlorine in a sealed tube, and opening it after it had stood for some days. The equilibrium conditions are illustrated by Fig. 135. The mobile, yellowish-brown liquid is rather redder in tint than sulphur dichloride. E. Beckmann said that the white powder begins to melt at −30°, and it is all liquid at −18°. A. Michaelis and O. Schifferdecker found that the compound rapidly dissociates when the temp. rises from −22° to −15°. O. Ruff and G. Fischer said that the tetrachloride melts at −30°, and as the temp. rises it gradually decomposes into sulphur monochloride and chlorine. The dissociation press. above the m.p. is only a little above one atm. Sulphur tetrachloride was found by A. Michaelis and O. Schifferdecker to be decomposed with the formation of sulphur dioxide and the separation of sulphur, and, added

O. Ruff, the hydrolysis is quantitative. When treated with sulphur trioxide, it forms thionyl chloride: $SCl_4+SO_3=SOCl_2+SO_2+Cl_2$, and some pyrosulphuryl chloride appears as a result of the action of sulphur trioxide on the thionyl chloride; sulphur dioxide has no action on the tetrachloride; while chlorosulphonic acid acts at 0° like sulphur trioxide, and below 0°, it forms pyrosulphuryl chloride. O. Ruff and G. Fischer could not make a compound of sulphur di- and tetra-chlorides. For K. Thiel's observations on the action of sulphur tetrachloride on arsenic and antimony trifluorides, silver fluoride, titanium tetrafluoride, stannic fluoride, and hydrogen fluoride, *vide supra*, sulphur tetrafluoride. V. Auger and A. Béhal found that sulphur tetrachloride reacts with acetic acid: $SCl_4+2CH_3COOH=2CH_3COCl+SO_2+2HCl$. The constitutional formula may be $Cl_4\equiv S:S\equiv Cl_4$, where sulphur is sexivalent. T. S. Moore regarded sulphur tetrachloride as an electrolyte, with the electronic structure:



$$\left[\begin{matrix} & & \ddot{\mathrm{Cl}} & & \\ :\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}} & : & \underset{\cdot\cdot}{\ddot{\mathrm{S}}} & : & \underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}: \end{matrix}\right]^{+}\left[:\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}:\right]^{-}$$

A number of complex salts with sulphur tetrachloride have been described. Thus, R. Weber prepared *iodine sulphoheptachloride*, $ICl_3.SCl_4$; O. Ruff, *iodine sulphodecachloride*, $2ICl_3.SCl_4$; L. Lindet, *gold sulphoheptachloride*, $AuCl_3.SCl_4$; R. Weber, *aluminium sulphodecachloride*, $2AlCl_3.SCl_4$; O. Ruff, *aluminium sulphoheptachloride*, $AlCl_3.SCl_4$; H. Rose, *titanium sulphododecachloride*, $2TiCl_4.SCl_4$; O. Ruff and G. Fischer, *titanium sulphoctochloride*, $TiCl_4.SCl_4$; O. Ruff, an impure *zirconium sulphochloride;* H. Rose, W. T. Casselmann, and O. Ruff and G. Fischer, *stannic disulphododecachloride*, $SnCl_4.2SCl_4$; O. Ruff, *arsenic sulphohexafluotetrachloride*, $2AsF_3.SCl_4$; H. Rose, R. Weber, O. Ruff and W. Plato, and O. Ruff and G. Fischer, *antimony sulphoenneachloride*, $SbCl_5.SCl_4$; and O. Ruff, *ferric sulphoheptachloride*, $FeCl_3.SCl_4$. O. Ruff observed that no complexes were obtained with antimony, tin, or titanium fluorides, or with the chlorides of the uni- or bi-valent metals. H. Rose said that the complexes he studied were all resolved by water into sulphurous and thiosulphuric acids, and that the latter was afterwards decomposed into sulphurous acid and sulphur.

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§ 48. Sulphur Bromides

A. J. Balard [1] observed that sulphur dissolves in bromine, forming a reddish-brown, oily liquid, lighter in colour than bromine, and darker than sulphur monochloride. This product, on exposure to air, gives off white fumes which smell like sulphur monochloride ; it reddens dry litmus very feebly, but moist litmus is strongly reddened ; it is slowly decomposed by cold water ; and with boiling water, the decomposition is sometimes attended with a slight explosion, forming hydrobromic, and sulphurous acids, and hydrogen sulphide. Chlorine decomposes it into sulphur chloride and bromine. H. Rose thought that it is doubtful if bromine forms a definite compound with sulphur, and if any such compound exists, it is decomposed by heat. The dissolution of pieces of sulphur in bromine is not attended by any sensible rise of temp. When a sat. soln. of sulphur in bromine, prepared at ordinary temp., is distilled at a gentle heat, the deep red distillate contains 10·43 per cent. of sulphur ; the fractions collected at successively higher temp. contained 21·99, 72·41, and 84·98 per cent. of sulphur, while the residue in the retort consists of dirty brown sulphur containing a little bromine. O. Ruff and G. Winterfeld obtained the m.p. of mixtures of bromine and sulphur monobromide, and found for the following percentages of bromine :

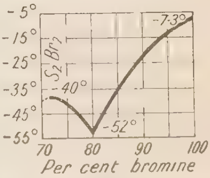

FIG. 140.—Portion of Melting-point Curve of Bromine and Sulphur.

Br .	71·38	75·71	80·51	85·08	90·37	93·03
M.p. .	−39·5°	−46°	−52°	−36°	−17·5°	−12·5°

The eutectic at about −52° has approximately 80 per cent. of bromine. Mixtures containing less than 71 per cent. of bromine did not give accurate results because of the undercooling followed by the separation of crystals of sulphur. The curve is quite regular and shows no indication of the existence of sulphur di- or tetrabromides, and a similar conclusion follows from the sp. gr., and vap. press. curves.

C. Löwig said that at ordinary temp. bromine dissolves about 30 per cent. of sulphur. This corresponds with what is required for **sulphur monobromide,** S_2Br_2. C. Löwig added that more sulphur is dissolved by bromine if the temp. is raised, but the excess separates out on cooling. M. M. P. Muir mixed stoichiometrical proportions of sulphur and bromine and by repeated fractionation obtained an impure monobromide with 70·39 instead of 71·38 per cent. of bromine. The monobromide is partially decomposed into its elements during distillation. According to O. Ruff and M. Wenzel, the pure monobromide can be obtained by heating the required proportions of the constituent elements in a sealed tube at 100°. The garnet-red liquid was distilled in vacuo, in thoroughly dried vessels, and the monobromide well protected from the moisture of the atm. E. Beckmann also obtained the monobromide by freezing a mixture of the two elements ; H. L. Snape, by heating sulphur dichloride with an excess of potassium bromide in a sealed tube ; and A. Besson, by heating thionyl bromide or chlorobromide in a sealed tube at 150° : $4SOBr_2=6Br+S_2Br_2+2SO_2$. G. Korndörfer obtained it by the action of hydrogen sulphide on bromine as a by-product in the preparation of hydrogen bromide.

G. Korndörfer observed that sulphur monobromide is a ruby-red, oily, heavy liquid which does not wet the glass walls of the containing vessel ; and, added M. M. P. Muir, it fumes slightly in air ; it reddens blue litmus ; and has an odour resembling that of sulphur monochloride. J. B. Hannay gave 2·62 at 4° for the **specific gravity.** As the sp. gr. of the mixed components is 2·515, the mixture is denser by 0·11 than is indicated by the mixture rule; there is therefore a 4·34 per cent. contraction on mixing the constituents. O. Ruff and G. Winterfeld gave 2·6355 for the sp. gr. at 20° and 762 mm. press., and for mixtures containing 80·88, 91·96, and 100 per cent. of total bromine respectively, 2·7896, 2·9650, and 3·1200. J. B. Hannay found the sp. gr. of mixtures in the following molar proportions; and the differences between the observed sp. gr. and those calculated by the mixture rule were:

	$S_3 : Br$	$S_2 : Br$	$S : Br$	$S : Br_2$	$S : Br_3$	$S : Br_4$
Sp. gr. .	2·293	2·425	2·628	2·820	2·880	2·905
Diff. .	0·011	0·065	0·108	0·150	0·129	0·125

Each increment of bromine doubles the increment in sp. gr. up to a maximum effect with $S : Br_2$; there is no sudden change at $S : Br$. I. I. Saslowsky studied the contraction which occurs when the monobromide is formed from its elements. The **melting point** is —40°. O. Ruff and G. Winterfeld's observations on the m.p. of mixtures of bromine and sulphur are indicated above, Fig. 140. J. B. Hannay observed that except when the proportion of bromine was very large, the mixtures would not freeze, but became thick like tar. It seems strange that mixtures of bromine and sulphur should remain liquid, below the temperature at which bromine freezes, yet this is the case: in fact SBr is quite liquid when bromine is solid. At temp. approaching —30° the mixture only becomes more viscid. Both H. Rose, and J. B. Hannay observed that on distilling the liquid obtained by mixing equi-atomic proportions of sulphur and bromine, it decomposes so that the first part of the distillate is nearly pure bromine, but the percentage of sulphur gradually increases with rise of temp. The liquid begins to boil at about 72°, but the **boiling point** rises continuously till the b.p. of sulphur is attained. By taking portions of the distillate between two selected temp., a distillate of any desired composition can be obtained. The largest proportion of the liquid distils over between 190° and 230°; and if this portion be redistilled, it does not yield a definite fraction with a fixed b.p. M. M. P. Muir found that by submitting the ruby-red monobromide to distillation, it began to boil at about 60°, and the temp. rose steadily until it neared 190°; it then slowly crept up to 200°; on reaching which point it again more quickly ascended to 220°; the residue in the retort now became nearly solid. The fraction 190° to 200°, collected separately, amounted to fully one-half of the entire liquid. The analysis of this fraction gave numbers in fair agreement with S_2Br_2, but on redistilling this liquid, dried by contact with calcium chloride, it continued to decompose so that a fraction boiling a few degrees lower than the first fraction contained 8 per cent. more bromine. Hence, it was concluded that at ordinary temp. sulphur and bromine unite to form a compound SBr or S_2Br_2; that heat causes a gradual dissociation of the mols. of this substance, but that even at 190°, mols. having the above atomic structure preponderate in the vapour; on removing the products of decomposition from the sphere of action, a further dissociation sets in, and these phenomena repeat themselves until the whole of the compound mols. are split up. If a current of dry carbon dioxide be passed for 6 hrs. at 15°, through a mixture of sulphur with more bromine than is needed to form the monobromide, the residue approximated fairly well with S_2Br_2; similar results were obtained at 50° and at 90°. The gradual dissociation of the monobromide is illustrated by J. B. Hannay's experiment in which dry air, at 16°, was passed through 5 grms. of the liquid monobromide, and the loss in grams measured after each passage of 4 litres per hour:

1	2	3	4	5	6	7	8	9	10 hrs.
0·0285	0·0282	0·0280	0·0275	0·0271	0·0263	0·0254	0·0246	0·0230	0·021

The total loss after 12 hrs.' treatment was 0·2985, showing that at 15° the monobromide can be completely dissociated in a current of air leaving a residue of sulphur.

O. Ruff and G. Winterfeld found for the **vapour pressure** of soln. of sulphur in bromine:

Br .	71·38	74·53	77·91	83·32	83·92	90·90	100·0 per cent.
p .	2·9	22·5	39·0	73·2	80·0	126·2	174·5 mm.

They observed that the monobromide can be distilled at 57°–58° and 0·22 mm. press.; at 54° and 0·18 mm.; and at 52·5° and 0·145 mm. press. W. Spring and A. Lecrenier inferred from the effect of sulphur monobromide on potassium sulphite—*vide supra*, sulphur monochloride—that it contains 27·11 per cent. of bromine in the free state, and the amount dissociated is greater, the more the composition deviates from S_2Br_2. G. Oddo and M. Tealdi observed that the **molecular weight** calculated from the effect on the f.p. of phosphoryl chloride corresponds with S_2Br_2; and E. Beckmann, and W. Finkelstein likewise from its effect on the f.p. of bromine. As indicated above, H. Rose observed that no sensible rise of temp. occurs when pieces of sulphur are dissolved in bromine; J. B. Hannay observed that in the formation of S_2Br_2 from its elements a little heat is evolved; and M. M. P. Muir added that when sulphur is added to bromine, the solid floats on the surface of the liquid and in time sinks down and is dissolved with but a slight rise of temp., whereas if the mixture be well shaken the sulphur dissolves very quickly with a considerable rise of temp. J. Ogier gave for the heat of formation, from solid sulphur, $(S_2,Br_2)=10{\cdot}0$, 2·0, and 1·8 Cals. respectively, with gaseous, liquid, and solid bromine. H. Becquerel gave 1·7360 for the **index of refraction,** and 1·942 for the **magnetic rotatory power** with red-light. O. Ruff and G. Winterfeld found that for the ray of wave-length 782 mm., the index of refraction $\mu=2{\cdot}6268$ calculated from $\mu=(N_2-\mathrm{Sin}^2\,\alpha)^{\frac{1}{2}}$, where $N=1{\cdot}62098$, and $\alpha=1^\circ\ 30'$. The **absorption spectrum** has a band in the red between 652 and 782 mm. with the maximum clearness at 782 mm. J. B. Hannay found that with soln. containing S : Br in the molar proportion 3 : 1, the spectrum of bromine above the liquid did not show the bromine lines below 42°; with the ratio 5 : 2, below 33°; 2 : 1, below 25°; 4 : 3, below 13°; 1 : 1, below 3°; 2 : 3, below −7°; and 1 : 2, the lines were visible at −18°. J. Plotnikoff found that a soln. of sulphur monochloride in bromine does not show any **electrical conductivity.** T. S. Moore regarded sulphur tetrachloride as an electrolyte.

M. M. P. Muir found that the properties of sulphur monobromide are such as would be expected from a comparative survey of the compounds of chlorine and bromine with the non-metallic elements, where the chlorides are more stable than the bromides, showing that chlorine exhibits a higher degree of chemical energy than bromine. J. B. Hannay found that when a thin layer of sulphur monochloride is exposed to **air** for a week so that moisture can act on it slowly, well-defined, octahedral crystals of sulphur—soluble in carbon disulphide—are deposited. Hence, if M. Berthelot be right in stating that electronegatively combined sulphur should deposit amorphous sulphur insoluble in carbon disulphide, it might be argued that the sulphur was not chemically combined with the bromine. The argument has no weight. C. Löwig, G. Korndörfer, and M. M. P. Muir observed that **water** decomposes sulphur monobromide into sulphur, and hydrobromic and sulphurous acids; the action is slow with cold water, and rapid with hot water. J. B. Hannay found that the monobromide reacts with iodine monochloride, forming sulphur monochloride, and iodine monobromide. According to H. Rose, a soln. of sulphur in bromine copiously absorbs **sulphur trioxide** without changing its appearance; it gives off no sulphur dioxide when distilled, and sulphur remains. The first distillate is a reddish-brown, fuming liquid which is freely soluble in water, forming bromine and hydrobromic and sulphuric acids; the later fraction is reddish-brown, and is liable to deposit sulphur but not to furnish free bromine. The liquid is slowly dissolved by water, forming hydrobromic and sulphuric acids. C. Löwig found that **ammonia** decomposes sulphur monobromide, forming nitrogen, sulphur, and ammonium bromide—*vide* sulphur monochloride. C. Löwig, and M. M. P. Muir observed that **nitric acid** attacks the monobromide violently, forming hydrobromic and sulphuric acids. C. Löwig said that when the monobromide is distilled with **phosphorus,** sulphur remains in the retort, and phosphorus tribromide distils over. J. B. Hannay found that sulphur monobromide has no visible action on red phosphorus, but white phosphorus is dissolved with the evolution of heat; when the cold, clear liquid is decanted from the phosphorus, and cautiously heated, just as it began to boil, " it seemed to take fire inside, and vivid combustion ensued for about a second, when the whole exploded with a brilliant flash and loud noise, shattering the apparatus and hurling the ignited combustible all about the room." M. M. P. Muir, and J. B. Hannay said that when the monobromide is dropped on powdered arsenic, great heat is evolved, and when the mixture is heated **arsenic** tribromide distils over. J. B. Hannay also found that powdered **antimony** behaves similarly; and when mixed with **methyl alcohol,** heat is evolved, sulphur precipitated, and a liquid with a sharp, sour odour is formed. A. Edinger and P. Goldberg found that sulphur monobromide can be used for brominating **organic compounds.** J. B. Hannay said that pieces of **sodium** or **potassium,** the size of half a pea, when dropped into sulphur monobromide, do not take fire, but quietly combine with the sulphur and bromine. If, on the other hand, they are very small or thin, they take fire, or at least hiss and become incandescent. **Aluminium** foil remains bright when immersed in sulphur monobromide; and C. Löwig said that when the vapour of the monobromide is passed over red-hot **iron,** bromide and sulphide of iron are formed with the evolution of heat and incandescence. G. Korndörfer represented the reaction with a soln. of **potassium hydroxide :** $2S_2Br_2+6KOH=4KBr+K_2SO_3+3S+3H_2O$; and with a soln. of **sodium hydrocarbonate :** $2S_2Br_2+6NaHCO_3=4NaBr+Na_2SO_3+6CO_2+3S+3H_2O$.

According to C. Löwig, the liquid formed on mixing equi-atomic proportions of sulphur and bromine contains sulphur monobromide, but on distillation, it breaks up into **sulphur dibromide,** SBr_2, and sulphur which remains in the retort. M. M. P. Muir said that no such compound is produced on distilling the monobromide —*vide supra*. While J. B. Hannay denied the existence of sulphur monobromide, S_2Br_2, he observed that the sp. gr. of mixtures of sulphur and bromine show a singular point when the proportions approach SBr_2. O. Ruff and G. Winterfeld observed no evidence of the existence of sulphur dibromide in their work in the f.p.—Fig. 138—the sp. gr., and the vap. press. of soln. of bromine in sulphur dibromide—*vide supra.*

A. Michaelis said that when sulphur dioxide acts on a mixture of phosphorus trichloride and bromine, at 115°, a dark-coloured liquid is formed containing **sulphur tetrabromide,** SBr_4, thus, $2PCl_3+Br_2+SO_2=2POCl_3+SBr_4$, and that the product immediately breaks down into sulphur monobromide and bromine. M. M. P. Muir, and O. Ruff and G. Winterfeld observed no evidence of the formation of the tetrabromide in their studies—*vide supra*—of the action of sulphur on bromine.

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§ 49. Sulphur Iodides

All the so-called sulphur iodides are probably only mixtures—*vide supra*, mol. wt. of sulphur in iodine. In 1813, B. Courtois,[1] in the first paper published on the properties of iodine, said: *le soufre s'unit à l'iode, mais avec moins d'energie que le phosphore*, and, a year later, J. L. Gay Lussac said that the combination of sulphur with iodine must be of the most feeble kind. He considered that there is some doubt as to the formation of a true chemical individual, when the two elements are heated together—even under water—and there is a slight rise of temp. The heat evolved is so small that it can be more reasonably attributed to the effect of mere soln. than to actual combination, for J. Ogier showed that the heat evolved when the alleged monoiodide is dissolved in carbon disulphide is equal to the sum of the heats of soln. of the elements separately in the solvent. F. C. Schlagdenhauffen said that "no heat is evolved, hence no chemical combination occurs." N. E. Henry described the preparation of *iodure de soufre* by fusing a mixture of the two elements. J. Inglis found that alcohol in a few months extracts all the iodine from the alleged iodides. H. Rose sublimed a mixture of the two elements, but the iodine so predominated in the sublimate that he concluded no true compound is formed; L. Lamers likewise could obtain no definite compound in this way. G. vom Rath, and H. L. Snape found that the crystals of the alleged monoiodide have all the characteristics of mixed crystals. F. Sestini, F. C. Schlagdenhauffen, and R. W. E. MacIvor investigated the m.p. of mixtures of iodine and sulphur, and concluded that the product obtained by fusion, or from soln. in a common solvent, has the characters of metal alloys, not true chemical individuals. C. E. Linebarger measured the m.p. of mixtures of sulphur and iodine, and obtained a curve, Fig. 141, which exhibited a maximum near that required for **sulphur monoiodide,** S_2I_2; he added that no indication of any other compound was obtained, and the monoiodide is in a very feeble state of combination, for the sulphur and iodine seem to have more tendency to form mol. aggregates than chemical combinations. On the other hand, R. Boulouch obtained no indication of any definite compound, or solid soln. in his examination of the m.p. and f.p. curves of mixtures of iodine and sulphur. This conclusion was confirmed by F. Ephraim, who found the following freezing points for mixtures containing the percentages of iodine by weight:

Iodine	100	86·8	72·9	55·5	52·3	51·5	36·6	24·8	12·7	0 per cent.
F.p.	112·8°	101·2°	89·2°	71·5°	65·7°	68°	74·3°	86·0°	97·9°	115·7°

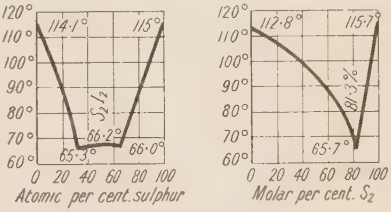

FIG. 141.—Melting-point Curves, and FIG. 142.—Freezing-point Curves of Mixtures of Iodine and Sulphur.

The results calculated for molar percentages are indicated in Fig. 142. The eutectic at 65·7° corresponds with 52·3 per cent. of sulphur by weight, or the molar per cent. 81·3. R. Boulouch gave for the eutectic 65·5 °and 51·1 per cent. of sulphur; and A. Smith and C. M. Carson, 65·6° and 51·1 per cent. of sulphur. R. Wright observed no signs of the formation of solid soln., or of chemical compounds of iodine and sulphur in his study of the vap. press. of the fused mixtures.

Sulphur iodides have been reported to be formed in several ways. J. Inglis believed that one is formed as a precipitate by the action of sulphur monochloride on hydriodic acid; R. de Grosourdy, by the action of hydrogen sulphide on a dil. soln. of potassium tetrachloroiodide; L. Lamers, and R. W. E. MacIvor—*sulphur ditritaiodide*, S_3I_2—by the action of hydrogen sulphide on iodine trichloride: $2ICl_3+3H_2S=6HCl+S_3I_2$; and M. Berthelot treated sulphur with dry hydrogen iodide in the cold: $2HI+(n+1)S=H_2S+S_nI_2$, the reaction is slow at ordinary temp., but faster at 100° or 500°. J. Ogier found that the heat of combination of sulphur and iodine *est très sensiblement null,* thus with solid sulphur the heats of formation of solid S_2I_2 are 10·8 and 0 Cals. with gaseous and solid iodine respectively; the heat of soln. of the alleged compound in carbon disulphide is the sum of the heats of soln. of the separate elements. W. Spring and A. Lecreiner made some observations on the oxidation of potassium sulphite—*vide supra,* sulphur monochloride—from which he estimated that the alleged S_2I_2 contains 90·12 per cent. of free iodine; S_2I_4, 88·89 per cent.; and SI_2, 89·97 per cent. The affinity of sulphur for chlorine is estimated to be 9·43 times that for iodine; and for bromine, 7·37 times that for iodine.

L. Lamers, and C. E. Linebarger obtained sulphur iodide by the slow evaporation of soln. of the two elements in carbon disulphide—the former represented his product by SI_6, and the latter by S_nI_n. J. Mori examined the equilibrium of iodine and sulphur in carbon disulphide soln. at 10° and 18°; no solid soln. were observed. M. Amadori measured the mutual solubility of iodine and sulphur in carbon disulphide, and found in grams per 100 grms. of soln. at 25°:

S .	34·76	36·42	39·56	40·82	36·74	12·83	—
I .	—	6·62	16·08	22·64	22·11	20·64	19·14
CS_2 .	65·24	58·96	44·40	36·48	41·15	66·53	80·86
Solid phase	Sulphur.				Iodine.		

The results are plotted in Fig. 143. The solubility curve consists of two branches meeting at the point of double saturation (two solid phases). Similarly with benzene as solvent; thus, at 25°, M. Amadori found:

S .	2·09	2·35	2·42	2·58	1·75	0·40	—
I .	—	8·31	12·72	16·42	16·28	16·08	15·79
CS_2 .	97·91	89·34	84·86	81·00	81·97	83·52	84·21
Solid phase	Sulphur.				Iodine.		

With bromoform as solvent, the soln. had 3·64 per cent. of sulphur and 3·22 per cent. of iodine at 5·6°; and 4·20 per cent. of sulphur and 3·70 per cent. of iodine at 3·65°. The solubility of one element in each of the three solvents is less than when the other element is present; and in the case of carbon disulphide, both solubilities are increased by more than 100 per cent. Cryoscopic measurements of mixtures of the two elements in bromoform show that the depression of the f.p. of the solvent is somewhat less than that calculated from the mol. wts. of the separate elements. No evidence was obtained of the existence of a solid compound of sulphur and iodine—nor did F. Ephraim observe any evidence of chemical combination in his measurements of the b.p. of soln. of the two elements. C. E. Linebarger found that the compound of sulphur and iodine is dissociated into molecular aggregates of the elements when in soln.; combination, if it occurs at all, intervenes during the act of crystallization. C. E. Linebarger added that there seems to be more affinity between sulphur atoms and iodine atoms to form complex elementary molecules than to enter into combination with each other.

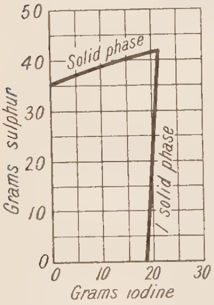

FIG. 143.—Mutual Solubility of Iodine and Sulphur in Carbon Disulphide.

The spontaneous evaporation of the soln. obtained by treating ethyl or other alkyl iodide with sulphur monochloride—best in a sealed tube for 12 hrs.—$2C_2H_5I+S_2Cl_2=2C_2H_5Cl+S_2I_2$, gave F. Guthrie what he regarded as sulphur monoiodide. F. C. Schlagdenhauffen confirmed this. The constant composition of the product is here not worth much as evidence of the individuality of the product because the two elements are necessarily in eq. proportions whether a monoiodide is formed or not. C. E. Linebarger obtained black, rhombic tablets of what he supposed to be S_nI_n in a similar manner. H. McLeod, however, said that the product has the nature of a metal alloy rather than of a chemical individual; and R. W. E. MacIvor based a similar conclusion on the facts that alcohol, potash-lye, or a soln. of potassium iodide extracts all the iodine from the alleged iodide, and the evaporation of a soln. of the alleged iodide in carbon disulphide furnishes crystals containing variable proportions of sulphur. A. E. Menke treated a soln. of an alkali iodide or hydriodic acid with sulphur dioxide, and obtained a yellow product thought to be the monoiodide: $8HI+2SO_2=4H_2O+3I_2+S_2I_2$; the precipitate is not stable and disappears when water is added.

L. Lamers reported crystals of what he called *sulphur hexaiodide*, SI_6, to be formed by the slow evaporation of mixed soln. of the constituent elements in carbon disulphide. G. vom Rath would have liked to call the resulting crystals isomorphous mixtures, but he hesitated to do so because of the dissimilarity of the two elements concerned. R. Schneider reported that crystals of *stannic disulphotetraiodide*, SnS_2I_4, are formed by sublimation from a mixture of a mol of stannic sulphide and 2 mols of iodine, or from a soln. of dry, precipitated stannic sulphide in a boiling soln. of iodine in carbon disulphide. He also prepared *arsenic trisulphohexaiodide*, $2AsI_3.As_2S_3$. F. Ephraim showed that the former is probably a mixture of stannic iodide, and sulphur; and the latter a mixture of arsenic trisulphide and iodine.

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§ 50. The Thionyl Halides

The bivalent radicle SO is called **thionyl.** It is derived from sulphurous acid, $SO(OH)_2$. If the chloride, $SOCl_2$, be treated with different fluorides—*e.g.* zinc fluoride—M. Meslans[1] found that **thionyl fluoride,** SOF_2, is formed. H. Moissan and P. Lebeau noticed that the same compound is formed, along with other oxyfluorides of sulphur, when fluorine acts on thionyl chloride; they prepared the compound by heating a mixture of 26·4 grms. of arsenic trifluoride and 35·7 grms. of thionyl chloride in a sealed tube for 30 min. at 100°; then cooled the tube and contents to −80°, and on opening the tube collected the gas which escaped over mercury. Traces of arsenic trifluoride and thionyl chloride can be removed by passing the gas through a tube cooled to −23°. The reaction is symbolized: $2AsF_3+3SOCl_2=3SOF_2+2AsCl_3$. W. Steinkopf and J. Herold used a modification of this process. O. Ruff and K. Thiel prepared the gas by heating nitrogen sulphide with hydrofluoric acid in the presence of water and cupric oxide in a sealed tube for 2 hrs. at 100°. The gas was scrubbed in a tube filled with sodium fluoride. F. Wunderlich obtained sulphuryl fluoride by heating a mixture of barium fluosulphonate and barium fluoride in a sealed tube at 150° whereby barium sulphate and sulphuryl fluoride were formed. O. Ruff and fellow-workers observed that antimony sulphofluoride decomposes in moist air, forming thionyl fluoride, which then decomposes into sulphurous and hydrofluoric acids.

Thionyl fluoride was described by H. Moissan and P. Lebeau as a colourless gas which fumes a little in moist air, and which has a suffocating odour. M. Meslans said that the gas attacks the respiratory organs vigorously. H. Moissan and

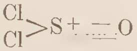
P. Lebeau found that the **specific gravity** of the liquid is 2·93; M. Meslans gave 3·0076, and he found that the gas liquefies at -30°. H. Moissan and P. Lebeau gave -32° for the **boiling point,** and O. Ruff and K. Thiel, -30° for the b.p. at 760 mm., and -110° for the **melting point.** When the gas is heated in a dry glass vessel to 400°, H. Moissan and P. Lebeau found that it decomposes $2SOF_2+SiO_2=SiF_4+2SO_2$; the action of the electric discharge from an induction coil on the gas in a glass vessel is similar to that of heat. O. Ruff and K. Thiel said that the gas is not changed when passed through a white-hot platinum tube filled with spongy platinum. H. Moissan and P. Lebeau found that if sparked along with **hydrogen** in a glass vessel, the sulphur dioxide is reduced to hydrogen sulphide, sulphur, and water, and the latter reacts with the silicon tetrafluoride, forming hydrofluosilicic acid. The presence of **oxygen** does not affect the decomposition of the thionyl fluoride by the action of heat, but when the mixture of the two gases is sparked, a certain amount of a more volatile oxyfluoride is produced—*vide infra,* sulphuryl fluoride. The gas is decomposed by **water:** $SOF_2+H_2O=SO_2+2HF$. O. Ruff and K. Thiel observed that a mixture of thionyl fluoride and **chlorine,** in a sealed glass tube, in sunlight, or in the presence of carbon, reacts with the silica of the glass to form silicon tetrafluoride and sulphuryl chloride. Under ordinary conditions chlorine, and **bromine** are inactive. H. Moissan and P. Lebeau found that when the gas is treated with **hydrogen chloride** over mercury, a gaseous mixture is produced which attacks the mercury. The gas is not attacked by **sulphur** at 500°, but, at high temp., **hydrogen sulphide** forms sulphur, water, and hydrogen fluoride; at ordinary temp., there is no reaction. M. Meslans found that the gas reacts with **ammonia,** forming ammonium fluoride and thionyl amide. F. Wunderlich represented the reaction: $SO_2F_2+4NH_3=2NH_4F+SO_2(NH_2)_2$. With **methylamine** in place of ammonia, he obtained dimethylsulphamide, $SO_2F_2+4CH_3NH_2=SO_2(NHCH_3)_2+2CH_3NH_3F$. Similarly, **ethylamine** furnishes diethylsulphamide. H. Moissan and P. Lebeau showed that the first product of the reaction with ammonia is an orange-coloured **thionyl hemipentamminofluoride,** $2SOF_2.5NH_3$, and finally a white substance corresponding with **thionyl hemiheptamminofluoride,** $2SOF_2.7H_2O$, and when the latter is treated with hydrogen chloride it forms sulphur, and sulphur dioxide. O. Ruff and K. Thiel said that thionyl fluoride reacts with **nitrogen trioxide** and moisture, forming nitrosulphonic acid; and silicon tetrafluoride; but the gas does not react with **nitric oxide.** H. Moissan and P. Lebeau observed no reaction with **phosphorus** at 500°. According to F. Wunderlich, one vol. of **glycerol** absorbs 0·12 vol. of the gas; **petroleum,** 1·4 vols.; **benzene,** 2·3 vols.; **toluene,** 2·9 vols.; **ethyl alcohol,** 3·0 vols.; **methyl alcohol,** 3·1 vols.; **carbon tetrachloride,** 3·4 vols.; **chloroform,** 4·0 vols.; and **acetone,** 4·9 vols.; while **ether** and **carbon disulphide** absorb only a little of the gas. H. Moissan and P. Lebeau also found that the gas is soluble in **arsenic trichloride,** and also in benzene, **turpentine,** and ether; and it is absorbed by molten **sodium** or **tin.** F. Wunderlich found that a soln. of **potassium sulphide** in absolute alcohol forms a little thiosulphate when treated with sulphuryl fluoride; and the reaction in an aq. soln. of **calcium hydrosulphide** is symbolized: $SO_2F_2+2Ca(SH)_2+H_2O=CaS_2O_3+CaF_2+3H_2S$.

J. Persoz and N. Bloch [2] first prepared **thionyl chloride,** $SOCl_2$, in an impure form, by the action of sulphur dioxide on phosphorus pentachloride; P. Kremers obtained it in a similar way, and named it *schwefligsaures Phosphorsuperchlorid* because it was supposed to have the composition $PCl_5.SO_2$ until H. Schiff prepared it in a fairly pure state and showed that its empirical composition is really $SOCl_2$. The work of L. Carius, C. A. Wurtz, and A. Michaelis demonstrated the chemical characteristics of the compound. C. Schorlemmer has made some remarks on the history of thionyl chloride. L. Carius prepared thionyl chloride by heating calcium sulphite with phosphoryl chloride to 150°. He first employed the proportions indicated in the equation: $3CaSO_3+2POCl_3=Ca_3(PO_4)_2+3SOCl_2$, and heated the mixture to 150° in sealed tubes; but so much sulphur dioxide was developed that the tubes burst. Possibly the reaction is $6CaSO_3+2POCl_3=Ca_3(PO_4)_2+3CaCl_2+6SO_2$, but some thionyl chloride is also formed. L. Carius found that by raising the proportion of oxychloride until equal molecular proportions of the two substances were present, the proportion of thionyl chloride greatly increased, and that of sulphur dioxide became very small. Calcium sulphite can thus be made to yield most of its sulphur as thionyl chloride, but only by using excess of phosphorus oxychloride, since without this excess sulphur dioxide is the main product. Now, this sulphur dioxide must be derived from thionyl chloride should phosphorus oxychloride really act on calcium sulphite, and then form thionyl chloride by this action. E. Divers and T. Shimidzu said that phosphorus pentachloride is itself without action on calcium sulphite, but at 150°, the pentachloride is dissociated into phosphorus pentoxide and pentachloride: $10POCl_3=2P_2O_5+6PCl_5$, the pentoxide takes calcium oxide from the sulphite, thus setting free sulphur dioxide: $6CaSO_3+2P_2O_5=2Ca_3(PO_4)_2+6SO_2$, and this with phosphorus pentachloride gives thionyl chloride and phosphorus oxychloride again: $6SO_2+6PCl_5=6SOCl_2+6POCl_3$—*vide infra*. Three-fifths of the phosphorus oxychloride begun with are thus regained. In practice, L. Carius found an extra half of the oxychloride to be excess enough to use. The large quantity of sulphur dioxide which forms when these proportions are greatly altered in favour of the calcium sulphite, is to be traced to the action of the phosphorus pentachloride upon the excess of calcium sulphite instead of upon the sulphur dioxide, as is shown by the following equation: $15CaSO_3+6PCl_5=3Ca_3(PO_4)_2+6CaCl_2+9SOCl_2+6SO_2$. With the other $6SO_2$ liberated, but now not decomposed, there are thus obtained $12SO_2$ to $9SOCl_2$. The calcium chloride here shown is a necessary complement to the sulphur dioxide, whatever version of the change be adopted. L. Carius also prepared thionyl chloride by the action of phosphorus pentachloride on sodium sulphite; and on certain organic sulphonates on the alkali metals; A. Michaelis made it by the action of phosphorus pentachloride on sulphuryl chloride; and K. Kraut, by its action on thiosulphates. J. Persoz and N. Bloch, P. Kremers, L. Carius, and H. Schiff prepared thionyl chloride by passing sulphur dioxide over phosphorus pentachloride—$SO_2+PCl_5=POCl_3+SOCl_2$—and separating the thionyl chloride—b.p. 82°—from the phosphoryl chloride—b.p. 110°—by fractional distillation. A. Michaelis said that chlorine and sulphur dioxide colour the product yellow, and they can be removed by boiling the liquid in a flask with a warm reflux condenser, and rejecting the first fraction. This mode of preparation was employed by T. E. Thorpe, and was formerly the process generally employed. The Chemische Fabrik von Heyden recommended making thionyl chloride by the interaction of phosphorus trichloride and sulphuryl chloride: $SO_2Cl_2+PCl_3=POCl_3+SOCl_2$; while the Chemische Fabrik von Buckan found that carbonyl chloride reacts with sulphur dioxide at temp. above 200° with the formation of thionyl chloride and sulphur tetrachloride according to the equations: $SO_2+COCl_2=SOCl_2+CO_2$ and $SO_2+2COCl_2=SCl_4+2CO_2$. The first reaction predominates at lower temp. and with excess of sulphur dioxide, and by suitable adjustment of conditions one or other of the reactions may be almost entirely excluded. The reactions are carried out by passing the gases over a heated contact substance, such as wood charcoal, and the carbonyl chloride may be partly or entirely replaced by a mixture of carbon monoxide and chloride, or carbon monoxide and sulphuryl chloride may be employed. This mode of preparation gives good results. The Farbenfabrik vorm. F. Bayer obtained thionyl chloride by heating a mixture of chlorosulphonic acid and sulphur monochloride or dichloride.

C. A. Wurtz observed that thionyl chloride is formed by the action of chlorine monoxide on sulphur, but the reaction proceeds with explosive violence; it was therefore found better to dissolve the sulphur in sulphur monochloride, and allow gaseous chlorine monoxide to act on the soln. at —12°, until nearly all the dissolved sulphur is consumed. The thionyl chloride and sulphur monochloride were separated by fractional distillation. C. A. Wurtz, and P. Schützenberger also obtained thionyl chloride by the action of chlorine monoxide on carbon disulphide : $3Cl_2O+CS_2=2SOCl_2+COCl_2$. A. Michaelis and O. Schifferdecker obtained an 80 per cent. yield of thionyl chloride by the action of sulphur trioxide on sulphur tetrachloride : $SCl_4+SO_3=SOCl_2+SO_2+Cl_2$; and A. Béhal and V. Auger, and W. Majert, by the action of sulphur trioxide on sulphur dichloride at a temp. below the b.p. of sulphur dioxide, or under press. : $SO_3+SCl_2=SOCl_2+SO_2$. The Chemische Fabrik Griesheim-Elektron obtained thionyl chloride by adding sulphur trioxide to ordinary sulphur chloride at a temp. of 75°–80°, according to $SO_3+S_2Cl_2=SOCl_2+SO_2+S$. Chlorine is passed in continuously in order to reconvert the sulphur produced into sulphur chloride. In this way, an almost theoretical yield is obtained, and the practical inconveniences attending the use of higher chlorides of sulphur are avoided. The Farbenfabriken vorm. F. Bayer found that the reaction proceeds smoothly at ordinary temp. and press., in the presence of antimony trichloride, mercuric chloride, or chlorides of the heavy metals ; and that sulphur or sulphur monochloride with chlorine and chlorosulphonic acid, or sulphur dichloride and chlorosulphonic acid can be used with or without the addition of the catalyst.

According to C. A. Silberrad, thionyl chloride may contain traces of phosphoryl chloride, stannic chloride, or sulphur di- or tri-oxide. The first of these contaminations was found by J. Ogier to be difficult if not impossible to remove. P. Lux detected stannic chloride by producing a yellow coloration with triphenylmethyl chloride, or a red coloration with *p*-triiododiphenylmethyl chloride—neither reagent gives the coloration with thionyl chloride alone. The stannic chloride can be removed by fractional distillation. H. Meyer and R. Turnau, and H. Meyer and K. Schlegel found that sulphur dioxide may be removed by distillation over dimethylaniline or quinoline, and colourless thionyl chloride may be obtained by distillation over linseed oil and purified beeswax. Thionyl chloride can be destroyed in mixtures where it is not desired by adding sufficient formic acid to react : $H.COOH+SOCl_2=2HCl+SO_2+CO$—a reaction discussed by C. Moureu, and H. Meyer and R. Turnau.

Thionyl chloride is a colourless, refractive liquid with a penetrating smell recalling that of sulphur dioxide. K. Heumann and P. Köchlin found the **vapour density** at 154° is 3·95, corresponding with the mol. $SOCl_2$ for which the theoretical density is 4·11 ; at 444·5°, the vap. density is about two-thirds the normal value, indicating that the compound is dissociating, and when the vapour is passed through a red-hot tube, the dissociation products are sulphur dioxide and monochloride, and chlorine. H. Standinger and W. Kreis also observed that when the vapour is chilled from 1000° to −190°, sulphur monochloride is formed. According to G. Oddo and E. Serra, the **molecular weight** calculated from the effect of the salt on freezing benzene is 108–110 ; and with boiling chloroform, 229–235, when the theoretical value for $SOCl_2$ is 119. When corrected with the results of G. Oddo to allow for volatilization in boiling soln. a normal value is obtained for the mol. wt. E. B. R. Prideaux represented the electronic structure :



$$\genfrac{}{}{0pt}{}{\mathrm{Cl}}{\mathrm{Cl}}\!>\mathrm{S}\,+\cdots\!=\!\mathrm{O}$$

A. F. O. Getman discussed thionyl chloride as a solvent. C. A. Wurtz gave 1·675 for the **specific gravity** at 0° ; G. Carrara and I. Zoppellari, 1·6577 at 1° ; R. Nasini, 1·655 at 10·4°/4° ; T. E. Thorpe found 1·6763 for the sp. gr. at 0°/4° ; and S. Sugden and co-workers gave 1·656 at 14·5°/4°, 1·622 at 32°/4°, and 1·593 at 48°/4°, or at θ°/4°, sp. gr. $=1\cdot683+0\cdot00188\theta$. T. E. Thorpe represented the **thermal expansion** $v=1+0\cdot00116419\theta+0\cdot0_6 91418\theta^2+0\cdot0_8 9536\theta^3$, where v represents the vol. attained when unit vol. at 0° is heated to θ° up to 78·8°. The sp. gr. at the b.p. is 1·52143, and the **molecular volume** 78·01. S. Sugden, and E. Rabinowitsch also studied the mol. vol. W. Ramsay and J. Shields obtained 30·80 and 27·22 dynes per cm. respectively at 19·8° and 45·9° for the **surface tension ;** $a^2=3\cdot83$ and 3·50 sq. mm. for the **specific cohesion** respectively at 19·8° and 45·9° ;

and 538·6 and 486·2 ergs. for the mol. **surface energy** at 19·8° and 45·9° respectively. H. A. Mayes and J. R. Partington gave −104·5° for the **freezing point.** C. A. Wurtz gave 78° at 746 mm. for the **boiling point ;** L. Carius, 82° ; and T. E. Thorpe, 78·8° ; S. Sugden and co-workers gave 76·9° to 77·1° at 772 mm. K. Arii gave $\log p=7{\cdot}60844-1648{\cdot}21\,T^{-1}$ for the vapour pressure. J. Ogier found the **specific heat** between 17° and 60° to be 0·2425 ; the **heat of vaporization,** 54·45 cals. per gram ; and the **heat of formation** for liquid thionyl chloride 47·2 Cals. P. Walden found that thionyl chloride is an ionizing solvent. R. Nasini found that the **indices of refraction** for the *F*-, *D*-, and *C*-rays to be respectively 1·544, 1·527, and 1·522. H. Schlundt gave 9·05 for the **dielectric constant** at 22°.

H. Schiff said that thionyl chloride is decomposed by **water,** and still more easily by soln. of alkali hydroxides, forming hydrochloric and sulphurous acids ; while L. Carius said that warm water, or no more than an equal vol. of cold water, furnishes sulphur and sulphuric acid. For the heterogeneous system G. Carrara and I. Zoppellari found the reaction between water and thionyl chloride at 1° could be represented by $(1/st)\log\{a/(a-x)\}=ak$, where s is the surface area of the liquids in contact ; a, the quantity of decomposable liquid ; x, the quantity of this liquid decomposed at the time t ; and k is a constant, 0·0152. W. Wardlaw and F. H. Clews assume that the reaction : $SOCl_2+H_2O\rightleftharpoons SO_2+2HCl$ is reversible, since H. S. Tasker and H. O. Jones found that when thionyl chloride acts on mercaptans at a low temp., 0° to −70°, hydrogen chloride and sulphur dioxide are evolved, and water is found among the residual products. H. B. North and A. M. Hageman found that **sodium dioxide** reacts violently with thionyl chloride at ordinary temp. : $2Na_2O_2+2SOCl_2=2NaCl+Na_2SO_4+SO_2Cl_2$, and $Na_2O_2+2SOCl_2=2NaCl+SO_2+SO_2Cl_2$, according to the proportions of reagents employed. With **barium dioxide** and a large excess of thionyl chloride in a sealed tube at 150°, the reaction is symbolized : $BaO_2+2SOCl_2=BaCl_2+SO_2+SO_2Cl_2$; but when mol. proportions are used : $2BaO_2+2SOCl_2=BaCl_2+BaSO_4+SO_2Cl_2$; **lead dioxide** and **manganese dioxide** act in a similar manner. Thionyl chloride is an active reducing and chlorinating agent. C. A. Silberrad said that the chlorine usually attaches itself to some portion of the substance acted upon, and the sulphur appears in combination with oxygen or chlorine. A. Besson found that thionyl chloride reacts with dry **hydrogen bromide,** forming thionyl bromide : $SOCl_2+2HBr=2HCl+SOBr_2$; and with dry **hydrogen iodide,** cooled by a freezing mixture, forming hydrogen chloride, sulphur dioxide, iodine, and sulphur : $2SOCl_2+4HI=4HCl+2I_2+SO_2+S$.

H. Prinz observed that when thionyl chloride is heated with **sulphur** at 180°, sulphur monochloride is formed. Here the oxygen of the thionyl chloride is not replaced by sulphur ; rather does the thionyl chloride behave like a mixture of sulphur dioxide and tetrachloride. O. Ruff said that thionyl chloride is indifferent towards sulphur even in the presence of aluminium chloride, and this behaviour can be used to separate it from sulphuryl chloride (*q.v.*). H. B. North and C. B. Conover represented the reaction above 150° by $2SOCl_2+3S=SO_2+2S_2Cl_2$. H. B. North and J. C. Thomson obtained similar results at 150°–180°. H. Prinz found that **hydrogen sulphide** does not react at ordinary temp., but at 60°, the reaction $2SOCl+2H_2S=4HCl+SO_2+3S$ occurs. A. Besson said that this reaction occurs slowly even when cooled in a mixture of ice and salt, and at a higher temp., the main reaction is $2SOCl_2+H_2S=S_2Cl_2+SO_2+2HCl$. O. Ruff said that the reaction between hydrogen sulphide and thionyl chloride is greatly accelerated if aluminium chloride be present. C. Moureu found that thionyl chloride does not at first mix with **sulphuric acid,** but after a time, hydrogen chloride and sulphur dioxide are given off ; and when the mixture is heated between 138°-157°, chlorosulphonic acid, and pyrosulphuryl chloride are the main products : $SOCl_2+H_2SO_4=SO_2+HCl+ClHSO_3$; and $3SOCl_2+2H_2SO_4=3SO_2+4HCl+S_2O_5Cl_2$. V. Lenher and H. B. North represented the reaction with **selenium :** $Se+2SOCl_2=SeCl_4+SO_2+S$; and with **selenium dioxide :** $SeO_2+2SOCl_2=SeCl_4+2SO_2$; the reaction was also studied by B. von Howath. V. Lenher and C. W. Hill found that tellurium tetrachloride is formed when an excess of thionyl chloride acts on **tellurium** or on **tellurium dioxide,** if not in excess, tellurium dichloride is formed.

H. Schiff at first thought that thionyl chloride reacts with **ammonia** to form thionyl amide, but later, A. Michaelis found that a mixture of nitrogen tetrasulphide, and ammonium chloride, sulphide, and polythionate is formed; and F. Ephraim and H. Piotrowsky observed that if thionyl chloride be slowly dropped into liquid ammonia, an intensely red soln. is formed which furnishes ammonium imidodisulphinate, $(NH_4)N(NH_4SO_2)_2$—*q.v.*—and it is a result of the hydrolysis of the imidosulphonamide, $HN(SONH_2)_2$, first formed. Some observations on the action of ammonia on thionyl chloride were made by M. Gurewitsch. According to F. Ephraim and H. Piotrowsky, sulphur is produced by the action of a conc. soln. of **hydrazine** on thionyl chloride, the sulphur then reacts with the excess of hydrazine $N_2H_4+2S=N_2+2H_2S$. With a dil. soln. of hydrazine, an unstable sulphurous hydrazide appears to be formed, but it has not been isolated. A. Mente found that an imidosulphonate is formed by the action of thionyl chloride on **ammonium carbamate.** C. Moureu observed that thionyl chloride reacts violently with **nitric acid** with the development of heat, and the formation of nitroxyl chloride, sulphur dioxide, and hydrogen chloride; nitrogen oxides and sulphuric acid are also formed in consequence of secondary reactions between the hydrogen chloride, the excess of nitric acid, and sulphur dioxide. T. E. Thorpe gave for the reaction with **silver nitrate :** $SOCl_2+AgNO_3=AgCl+Cl.SO_2.O.N:O$. H. B. North and J. C. Thomson found that with an excess of thionyl chloride, **phosphorus** reacts: $2P+4SOCl_2=2PCl_3+2SO_2+S_2Cl_2$ after 2 hrs.' heating at 125°; if the temp. be 180°, some phosphorus pentachloride is formed as indicated below. A. Besson said that gaseous **phosphine,** at ordinary temp., reacts with thionyl chloride causing an evolution of hydrogen chloride, the liquid after some time forms two layers, the upper of which, on distillation under reduced press., yields, first, thionyl chloride, then phosphoryl chloride, and, finally, thiophosphoryl chloride, $PSCl_3$; a syrupy liquid from which no definite compound can be obtained remains in the retort. The lower layer is viscous, and contains chlorine, sulphur, phosphorus, oxygen, and hydrogen. C. Moureu found that ortho- and meta- **phosphoric acids** are at once attacked by thionyl chloride, but with metaphosphoric acid the reaction is incomplete, and orthophosphoric acid furnishes chlorinated condensation products which are not further attacked by thionyl chloride. D. Balareff found that boiling thionyl chloride converts orthophosphoric acid into a mixture of the pyro- and meta-acids. L. Carius represented the reaction with **phosphorus pentasulphide** at 150°: $5SOCl_2+P_2S_5=5S_2Cl_2+P_2O_5$, but H. Prinz showed that the reaction is more probably: $2P_2S_5+6SOCl_2=4PSCl_3+3SO_2+9S$, at temp. below 150°, and A. Michaelis found that the reaction, at 160°, with **phosphorus trichloride :** $3PCl_3+SOCl_2=PCl_5+POCl_3+PSCl_3$, is slow but complete—H. B. North and J. C. Thomson said incomplete in 16 hrs. at 80°–160°; possibly with an excess of thionyl chloride, there is a secondary reaction: $3PCl_3+4SOCl_2=3PCl_3+2SO_3+S_2Cl_2$. H. B. North and A. M. Hageman represented the reaction with **arsenic :** $2As+4SOCl_2=2AsCl_3+S_2Cl_2+2SO_2$; and with **arsenic trioxide,** the trichloride is formed. H. B. North and C. B. Conover represented the reaction with **arsenic trisulphide :** $As_2S_3+6SOCl_2=2AsCl_3+3SO_2+3S_2Cl_2$, and similar remarks apply to *orpiment.* K. Heumann and P. Köchlin represented the reaction with powdered **antimony** in the cold: $6Sb+6SOCl_2=4SbCl_3+Sb_2S_3+3SO_2$. H. B. North and A. M. Hageman agreed with this statement provided the antimony is in excess, and the reaction occurs with violence at ordinary temp. If heated in a sealed tube with a large excess of thionyl chloride, the **antimony trichloride** first formed reacts: $3SbCl_3+4SOCl_2=3SbCl_5+S_2Cl_2+2SO_2$. With **antimony trioxide** at ordinary temp., antimony trichloride, and with an excess of thionyl chloride, heated in a sealed tube at 150°–250°, antimony pentachloride is formed. H. Prinz represented the reaction with **antimony trisulphide :** $6SOCl_2+2Sb_2S_3=4SbCl_3+9S+3SO_2$. This was probably below 150°

and without excess of thionyl chloride, because H. B. North and C. B. Conover showed that the thionyl chloride reacts with the sulphur above this temp., and between 150° and 200°, the reaction in symbolized: $6SOCl_2+Sb_2S_3=2SbCl_3+3SO_2+3S_2Cl_2$. Similar remarks apply to *stibnite*. The reaction with **bismuth** at 200° is symbolized: $2Bi+4SOCl_2=2BiCl_3+S_2Cl_2+2SO_2$; and with **bismuth trioxide**: $Bi_2O_3+3SOCl_2=2BiCl_3+3SO_2$. C. Moureu found that the action of thionyl chloride on **boric acid** resembles that with orthophosphoric acid.

H. S. Tasker and H. O. Jones found that the reaction of thionyl chloride with **nickel carbonyl** results in the vigorous evolution of sulphur dioxide and carbon monoxide accompanied by a fall of temp.: $2Ni(CO)_4+2SOCl_2=2NiCl_2+SO_2+8CO+S$. In many reactions thionyl chloride behaves as if it were a mixture of sulphur dichloride, SCl_2, and sulphuryl chloride, SO_2Cl_2. The reactions of thionyl chloride with **organic compounds** have been summarized by C. A. Silberrad. He classifies the reactions: (i) *The replacement of various radicles or of oxygen or hydrogen by chlorine.* Thus, the replacement of hydroxyl, OH, was observed by G. Barger and A. J. Ewins, A. Stähler and E. Schirm, A. McKenzie and T. M. A. Tudhope, A. McKenzie and F. Barrow, A. McKenzie and G. W. Clough, L. McMaster and F. F. Ahmann, G. Darzens, L. Ruzicka and F. Liebl, H. Wieland and P. Kappelmeier, P. F. Frankland and F. H. Garner, A. Green, E. E. Blaise and M. Montagne, etc. The replacement of thiol, SH, was observed by O. Silberrad; the nitro- or NO_2-group, by H. Meyer; the sulphonic- or HSO_3-group, by H. Meyer, J. Pollak and B. Schadler, and J. Pollak and Z. Rudich; of hydrogen, by A. Michaelis, G. Schröter and E. Linow, J. Pollak and Z. Rudich, and H. Meyer; and of oxygen, by H. Hunter, P. Höring and F. Baum, and F. Loth and A. Michaelis. (ii) *The introduction of sulphur alone or in combination with oxygen to form SO-groups. E.g.*, the formation of sulphurous esters was observed by L. Carius, A. Michaelis and G. Wagner, A. Rosenheim and W. Sarow, A. E. Arbusoff, H. Hunter, L. Ruzicka and F. Liebl, A. McKenzie and G. W. Clough, M. M. Richter, and A. Green; the formation of thionyl derivatives—sulphoxides—by C. E. Colby and C. S. McLoughlin, H. C. Parker, S. Smiles and A. W. Bain, S. Smiles and R. le Rossignol, E. Schiller, P. F. Frankland and F. H. Garner, W. S. Denham and H. Woodhouse, A. Michaelis, A. Michaelis and R. Herz, A. Michaelis and W. Jacobi, A. Michaelis and O. Storbeck, G. Schröter and E. Linow, A. Michaelis and G. Schröter, A. Michaelis and G. Erdmann, A. Michaelis and J. Ruhl, A. Michaelis and P. Gräntz, and A. Francke; the formation of anhydrosulphites, by K. Moers, M. M. Richter, and E. E. Blaise and M. Montagne; and the replacement of hydrogen by sulphur to form a sulphide, by A. Michaelis, A. Michaelis and E. Godchaux, A. Michaelis and B. Philips, A. Michaelis and P. Schindler, C. T. Sprague, G. Tassinari, and H. Voswinckel. (iii) *Dehydration by the removal of the elements of water. E.g.*, E. de B. Barnett and I. G. Nixon, A. Michaelis and H. Sieber, H. Meyer, G. Lasch, B. von Pawlewsky, A. Wohl, A. McKenzie and T. M. A. Tudhope, C. Moureu, P. Höring and F. Baum, W. Herre, G. Schröter and M. Lewinsky, and M. Bergmann and A. Miekeley. (iv) *Dehydrogenation by the removal of hydrogen. E.g.*, B. Holmberg, H. S. Tasker and H. O. Jones, J. A. Smythe and A. Forster, and K. A. Hofmann and K. Ott. (v) *Condensations. E.g.*, S. Smiles and R. le Rossignol, G. Barger and A. J. Ewins, A. Michaelis and G. Erdmann, and P. Freundler. (vi) *Catalytic actions.* The presence of thionyl chloride was found to favour a number of reactions —F. G. Mann and co-workers, A. Shimomura and J. B. Cohen, R. S. Bly and co-workers, R. Wolffenstein and F. Hartwich, H. Meyer, K. H. Meyer and K. Schuster, G. Egerer-Seham and H. Meyer, S. Jaroschy, C. L. Horton, A. McKenzie and G. W. Clough, G. W. Clough, and P. Karrer and W. Kaase. (vii) *Other reactions* have been investigated by J. Klieeisen, H. McCombie and H. A. Scarborough, H. Meyer and K. Schlegel, H. Meyer and R. Turnau, G. Sachs, R. Stümmer, B. Singh and J. F. Thorpe, E. de B. Barnett and J. W. Cook, H. Leuchs, C. Böttinger, etc.

Thionyl chloride reacts with many of the **metals**—cold or hot—forming chlorides with the evolution of heat. H. B. North and A. M. Hageman said that at temp. up to about 250°, the reaction with bivalent metals is symbolized: $3M+4SOCl_2=3MCl_2+2SO_2+S_2Cl_2$, if the thionyl chloride is in excess, and if the metal is in excess, $3M+2SOCl_2=2MCl_2+MS+SO_2$. They found that **gold** is not attacked at temp. up to 150°, but at 200° it slowly forms auric chloride; **magnesium, zinc,** and **cadmium** are not attacked by thionyl chloride at 200°; but E. Fromm and J. de Seixas-Palma found that the reaction with zinc dust can be represented by $2SOCl_2+2Zn=2ZnCl_2+SO_2+S$. H. B. North found that **mercury** with thionyl chloride in a sealed tube at 150° reacts either $Hg+4SOCl_2=HgCl_2+2SO_2Cl_2+S_2Cl_2$, or $3Hg+4SOCl_2=3HgCl_2+2SO_2+S_2Cl_2$ according to the proportions of the reagents. The reaction with **tin** furnishes stannous chloride: $3Sn+2SOCl_2=2SnCl_2+SnS+SO_2$, but in the presence of an excess of thionyl chloride some **stannous chloride** is converted into stannic chloride: $3SnCl_2+4SOCl_2=3SnCl_4+2SO_2+S_2Cl_2$. Neither **lead** nor **chromium** is attacked at 200°; the reaction with **iron** is symbolized: $2Fe+4SOCl_2=2FeCl_3+2SO_2+S_2Cl_2$, and with an excess of metal: $3Fe+2SOCl_2=2FeCl_2+FeS+SO_2$; **nickel** is not attacked at 200°. Several **metal oxides** are converted into chlorides or oxychlorides with the evolution of sulphur dioxide. G. Darzens and F. Bourion said that at temp. below 400°, thionyl chloride behaves towards metal oxides like a mixture of chlorine and sulphur monochloride, but it is less advantageous in practice as a chlorinating agent owing to the difficulty of obtaining it free from phosphorus compounds. H. B. North and A. M. Hageman said that at 150°–250°, the metal oxides react: $MO+SOCl_2=MCl_2+SO_2$; and with a metal forming two chlorides, the lower chloride is first formed, and this is then oxidized to the higher chloride: $3MCl_2+4SOCl_2=3MCl_4+2SO_2+S_2Cl_2$. They found that **cupric oxide** reacts: $CuO+SOCl_2=CuCl_2+SO_2$; and **cuprous oxide**: $Cu_2O+3SOCl_2=2CuCl_2+SCl_2+2SO_2$. Only a trace of chloride is produced when thionyl chloride reacts with **silver oxide** under these conditions; **calcium, strontium,** and **barium oxides** are not attacked by thionyl chloride at 200°, nor is beryllium oxide attacked; **magnesium oxide** reacts: $MgO+SOCl_2=MgCl_2+SO_2$; and **zinc and cadmium oxides** react in an analogous manner. In a sealed tube at 160°, H. B. North found that **mercuric oxide** reacts: $HgO+3SOCl_2=HgCl_2+SO_2Cl_2+S_2Cl_2$, but if the thionyl chloride be not present in large excess: $HgO+SOCl_2=HgCl_2+SO_2$. H. B. North and A. M. Hageman found that **aluminium and chromic oxides** are not attacked by thionyl chloride at 200°; G. Darzens and F. Bourion found that at a higher temp. chromic oxide forms the chloride and with **lanthanum, samarium, zirconium,** and **thorium oxides,** the anhydrous chloride is also produced, but with **tungstic and vanadic oxides,** oxychlorides are formed; and with **titanic oxide,** a sulphochloride was formed, and with **gadolinium oxide,** a mixture of chloride and oxychloride was formed. H. B. North and A. M. Hageman said that **tin dioxide** is not attacked at 200°. H. B. North and C. B. Conover said that the reaction with **metal sulphides** at 150°–180° can generally be represented by $MS+2SOCl_2=MCl_2+SO_2+S_2Cl_2$; for example, this reaction applies to copper, silver, zinc, cadmium, and mercuric sulphides; similar remarks apply to *covellite, argentite, sphalerite,* and *cinnabar* and to *galena* or lead sulphide; with stannic sulphide the reaction is $SnS_2+4SOCl_2=SnCl_4+2SO_2+2S_2Cl_2$; and with ferrous sulphide there is a complication owing to the oxidation from the ferrous to ferric state: $6FeS+16SOCl_2=6FeCl_3+8SO_2+7S_2Cl_2$. They found that while the minerals argentite, *molybdenite*, and *cobaltite* were not attacked by thionyl chloride in a sealed tube at 150°–175°, a few hours' heating decomposes galena, *pyrites*, cinnabar, orpiment, stibnite, and *arsenical pyrites*, while *pyrargyrite, proustite*, covellite, sphalerite, and *tetrahedrite* require one to two days for their decomposition.

According to A. Michaelis,[3] **thionyl bromide,** $SOBr_2$, is produced by the action of bromine on thionyl aniline: $C_6H_5.N:SO+3Br_2=C_6H_2Br_3NH_2.HBr+SOBr_2$. He said that the brown liquid product is difficult to purify. This was confirmed by H. A. Mayes and J. R. Partington. P. J. Hartog and W. E. Sims prepared it by the interaction of sodium bromide and thionyl chloride. H. A. Mayes and J. R. Partington said that the action with potassium bromide is slow, and the large bulk of solid renders the first distillation in vacuo very awkward. A. Besson found that while dry hydrogen bromide has no action on thionyl chloride in the cold, the reaction at the b.p. results in the partial substitution of the chlorine by bromine. The fractional distillation of the product under reduced press. furnished thionyl bromide, and chlorobromide. H. A. Mayes and J. R. Partington prepared thionyl bromide by this process. A. Besson later obtained the same products by the action of aluminium bromide on thionyl chloride. The reaction is vigorous, and when the soln. is cooled, crystalline complex compounds of aluminium chloride and bromide with thionyl chloride are deposited. When the product is distilled under reduced press. it furnishes thionyl bromide. A better yield is obtained by the action of dry hydrogen bromide on thionyl chloride at a temp. not exceeding 100°. When the product is distilled under reduced press., it furnishes thionyl bromide, boiling at 68° under a press. of 40 mm.; the higher boiling fraction, thionyl chlorobromide; and sulphur bromide are also separated by fractional distillation. A. Besson said that thionyl bromide is not formed by the action of sulphur dioxide on phosphorus pentabromide. H. A. Mayes and J. R. Partington found that the reaction which occurs on adding the calculated quantity of sulphur trioxide to cooled sulphur bromide results in a violent effervescence: $S_2Br_2+SO_3=SOBr_2+SO_2+S$. The distillation of the product furnishes unchanged sulphur monobromide, and so little thionyl bromide that the method is useless as a mode of preparing thionyl bromide. Thionyl bromide was said by P. J. Hartog and W. E. Sims to be a deep crimson liquid; A. Michaelis, a brown liquid—but these liquids were probably contaminated with sulphur bromides, and bromine, since A. Besson found it to be a pale yellow liquid. P. J. Hartog and W. E. Sims said that the sp. gr. of the hygroscopic liquid is 2·6 at 18°, and A. Besson, 2·61 at 0°. H. A. Mayes and J. R. Partington said that the yellowish-orange liquid has a sp. gr. 2·697 at 15°/4°, 2·692 at 17°/4°, and 2·672 at 25°/4°. The surface tension at 17° is 43·71 dynes per cm., and at 25°, 43·08 dynes per cm. The results are in agreement with a small degree of association. A. Besson added that the liquid does not solidify at —23°, but does so at —50°; H. A. Mayes and J. R. Partington gave —52° for the f.p. A. Besson found that thionyl bromide boils at 68° under a press. of 40 mm. H. A. Mayes and J. R. Partington found for the b.p. at different press., p mm.,

p	22	47	104	138·5	219	315·5	471	680	773
B.p.	45°	62·5°	81·5°	90°	101·5°	111°	123·5°	136°	138°

The ratios of the b.p. at different press. indicates a little dissociation. The mol. wt., calculated from the action of thionyl bromide on the f.p. of benzene, agrees with the assumption that 25 per cent. exist as doubled molecules. The mol. heat of vaporization is 10·4 Cals., and Trouton's coefficient, 25·2 points to some association of the liquid. Unlike P. J. Hartog and W. E. Sims, H. A. Mayes and J. R. Partington were able to keep thionyl bromide in a stoppered bottle without decomposition for a few weeks; but decomposition does occur, and the thionyl bromide acquires a red colour owing to the formation of free bromine. About one-third decomposes: $4SOBr_2=2SO_2+S_2Br_2+3Br_2$, when the liquid is distilled at ordinary press. At a temp. a little above its b.p.—at 136°, according to A. Michaelis, and at 150°, according to P. J. Hartog and W. E. Sims—it decomposes into sulphur monobromide, bromine, and sulphur dioxide. H. Staudinger and W. Kreis observed that when the vapour is suddenly chilled from 100° to —190° bromine, sulphur, and sulphur dioxide appear. A. Besson added that thionyl bromide is rapidly decomposed by water; and in contact with mercury it yields sulphur, sulphur dioxide, and mercurous bromide. H. A. Mayes and J. R. Partington said that thionyl bromide is a very reactive liquid attacking both cork and rubber very readily. It is soluble in the more inert organic solvents—*e.g.* benzene, carbon disulphide, carbon tetrachloride, and chloroform. It reacts vigorously with acetone, forming a vapour which has a very irritating effect on the eyes; with organic acids it forms acid bromides just as thionyl chloride gives acid chlorides. The corresponding *thionyl iodide*, SOI_2, has not been prepared.

A. Besson reported **thionyl chlorobromide,** SOClBr, to be formed as just indicated. It is described as a pale yellow liquid which boils and slightly decomposes at about 115° under normal press., and does not solidify at —23°; the sp. gr. =2·31 at 0°. At a temp. a little above its b.p., it decomposes into sulphur dioxide, thionyl chloride, bromine, and sulphur bromide, and the same decomposition takes place slowly in the cold. The chlorobromide is rapidly decomposed by water. In contact with mercury, thionyl chloride and mercurous bromide are formed, sulphur is liberated, and sulphur dioxide is given off. H. A. Mayes and J. R. Partington measured the f.p. of mixtures of thionyl chloride and bromide, and the results are illustrated by Fig. 144. The simple mixed-crystal curve shows a minimum, but no eutectic. They were also unable to establish the existence of thionyl chlorobromide as a bromination product of thionyl chloride because (i) it is impossible to separate any constant-boiling liquid, other than thionyl chloride and thionyl bromide, from the product of bromination of thionyl chloride with hydrogen bromide. (ii) The freezing-point curve shows that no intermediate compound is present in mixtures of thionyl chloride and bromide. (iii) Physical properties show that the product of bromination of thionyl chloride is exactly the same as mere mixtures of thionyl chloride and bromide.

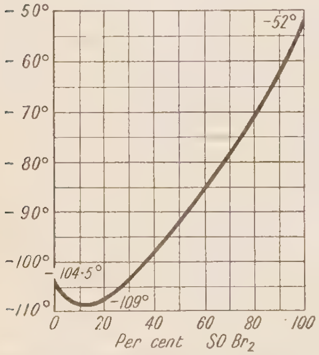


Fig. 144.—Freezing-point Curves of Mixtures of Thionyl Chloride and Bromide.

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§ 51. Sulphuryl Halides

H. Moissan and P. Lebeau[1] prepared **sulphuryl fluoride,** SO_2F_2, by passing fluorine into an apparatus containing sulphur dioxide so disposed that the former gas as it reaches the latter is strongly heated by means of a platinum wire placed at the inner end of the inlet tube and rendered incandescent by an electric current. Without this device, the combination of the gases is delayed, and then subsequently takes place with explosive violence. The gas may also be obtained by passing fluorine into moist hydrogen sulphide, when the former burns quietly with a blue flame; the product also contains silicon tetrafluoride, sulphur hexafluoride, and thionyl fluoride; when the experiment is performed in glass vessels, the presence of moisture is not essential, the necessary oxygen being derived from the action of the hydrogen fluoride produced on the silica. The sulphuryl fluoride, freed from the other products by washing with water and with copper sulphate soln., is dried over fused potassium fluoride, liquefied, and fractionated in vacuo. O. Ruff did not agree with T. E. Thorpe and W. Kirman's assumption that sulphuryl fluoride is formed by boiling fluosulphonic acid: $2F(HSO_3)=SO_2F_2+H_2SO_4$, because the acid is stable up to 900°; but W. Traube said that sulphuryl fluoride is probably formed when sodium fluosulphonate is heated in an atm. of carbon dioxide: $2NaSO_3F=Na_2SO_4+SO_2F_2$; and W. Traube and co-workers said that the most convenient way of making sulphuryl fluoride is to heat barium fluosulphonate to redness.

Sulphuryl fluoride is said to be a very stable compound which at ordinary temp. occurs as a colourless, odourless gas; which liquefies at $-52°$, and solidifies in liquid oxygen. The **vapour density** at 15° is 3·55 when the value calculated for SO_2F_2 is 3·53. The **melting point** is $-120°$, and the vapour press. at $-120°$ is 65 mm., and at $-80°$, 241 mm. The **boiling point** is $-52°$. The gas is stable at temp. below dull redness, but when strongly heated in glass vessels, it interacts with the silica, forming silicon tetrafluoride and sulphur di- and tri-oxides. When mixed with **hydrogen,** and heated to redness, a white solid is formed, yielding sulphuric and hydrochloric acids when treated with water. The gas is but slightly decomposed by **oxygen** even when aided by the electric spark; the gas has no action on **water** at 150°; one part of the gas dissolves in 10 parts of water at 9°. **Fluorine** has no action even at 200°; **hydrogen chloride** has no action at a dull red-heat; **sulphur** readily decomposes the gas at a red-heat in glass vessels, forming silicon tetrafluoride and sulphur dioxide; **selenium** acts like sulphur; **hydrogen fluoride** at a dull red-heat gives a deposit of sulphur; **sulphuric acid** does not dissolve the gas; **ammonia** at ordinary temp. forms **sulphuryl pentamminofluoride,** $SO_2F_2.5NH_3$, which is soluble in water. Sulphuryl fluoride has no action on **phosphorus;** neither does it act on **arsenic; carbon** behaves similarly; **alcohol** absorbs three times its vol. of the gas at 9°; **boron** has no action; **silicon** slightly decomposes the gas, but the reaction is not complete in an hour; fused **sodium,** and **calcium** completely absorb the gas, forming the corresponding sulphides and fluorides; **magnesium,** and **iron** have no action even at a red-heat; an aq. soln. of **potassium, calcium, or barium hydroxide** slowly absorbs the gas, but an alcoholic soln. of an alkali hydroxide rapidly absorbs the gas.

In 1838, in his memoir: *Sur l'acide chlorosulfurique et la sulfamide,* H. V. Regnault[2] described how a mixture of equal vols. of chlorine and sulphur dioxide when exposed to sunlight, produces fumes which in the course of a few days condense for the most part to a liquid. This liquid may be purified by distillation over mercury, rejecting the first fraction, since it may contain sulphur dioxide. The product is **sulphuryl chloride,** SO_2Cl_2. A. Coehn and H. Tramm, and J. Cathala found that the reaction is completely inhibited by the intensive drying of the gas. M. Trautz observed that the attainment of equilibrium in the balanced reaction: $SO_2Cl_2 \rightleftharpoons SO_2+Cl_2$ is accelerated by animal charcoal, but not by cocoa-nut charcoal to any marked degree; and W. J. Pope showed that bone charcoal or activated wood charcoal is a convenient catalyst for promoting the union of the two gases to form sulphuryl chloride. Combination occurs instantaneously when the reaction vessel is cooled to 30°—E. Terlinck recommended $-10°$—and the chloride is condensed and can be drained away as rapidly as it is formed. No limit to the life of the catalyst has been observed. The subject was discussed by R. H. McKee and C. M. Salls, E. Schering, E. Terlinck, and F. Bayer and Co. According to H. Danneel, sulphuryl chloride is easily prepared by the interaction of sulphur dioxide and chlorine in presence of activated carbon if provision is made for removing the heat of reaction, *e.g.*, by allowing the catalyst tube to fill with liquid sulphuryl chloride and cooling externally. The sulphuryl chloride overflows as it is formed through a side tube into a collecting vessel, a yield of 100 per cent. being readily obtained. In the system $SO_2Cl_2 \rightleftharpoons Cl + SO_2$, it was found that the percentage dissociation, α,

	102°	109°	110·6°	136·8°	158·6°	176·8°	178·5°	191·1°
α .	91·24	92·82	94·00	96·68	97·30	98·00	98·04	98·20

The equilibrium constant K in $K[SO_2Cl_2]=[SO_2][Cl_2]$ is given by $\log K=-2254{\cdot}2T^{-1}+1{\cdot}75\log T-0{\cdot}000455T+C$. The calculated value for C is 3·32, but the observed values are between 2·98 and 1·35. S. Dushman, C. N. Hinshelwood and C. R. Prichard, and D. Alexejeff made observations on this subject. C. N. Hinshelwood and C. R. Prichard showed that the reaction occurs mainly in the walls of the containing vessel. D. F. Smith found that the velocity of decomposition is a first order homogeneous reaction, and can be represented by $-dp/dt=kp$, where at 289·3°, 299·5°, 320·1°, and 339·4° the values of $k\times10^5$ are respectively 6·09, 27·1, 132·1, and 274·2. M. Trautz and D. S. Bhandarkar assumed that the dissociation of a mol. depends on the number of collisions between its constituent parts, and they derive $k=8{\cdot}72\times10^4\sigma^{-1}\{(A+B)/AB\}^{\frac{1}{2}}T^2{}_{\iota}-Q/RT$, where σ represents the mean diameter of the reacting molecules; A, the mol. wt. of sulphur dioxide; and B, that of chlorine. D. F. Smith found values of Q calculated by this equation gave satisfactory results. Y. K. Sirkin found that the quantum theory—**4**. 25, 8—did not apply to the decomposition of sulphuryl chloride. H. L. F. Melsens obtained sulphuryl chloride, without the aid of sunlight, by passing sulphur dioxide and chlorine into glacial acetic acid, and separating the sulphuryl chloride from the chloracetic acid, simultaneously formed, by fractional distillation; and it is also formed by the action of sulphur dioxide on carbon saturated with chlorine. According to H. Schulze, the presence of ethylene, charcoal, glacial acetic acid, and camphor accelerate the union of the two gases in the absence of sunlight. By passing sulphur dioxide and chlorine gases alternately through a flask containing a small quantity of camphor, say 5 grms., a large quantity of sulphuryl chloride can be easily prepared—*e.g.* 472 grms. after 15 operations when the action had almost ceased. V. Thomas and P. Dupuis said that sulphur dioxide unites with liquid chlorine. The Badische Anilin- und Sodafabrik prepared sulphuryl chloride industrially by dissolving some camphor in liquid sulphur dioxide, and then adding the calculated quantity of liquid chlorine. The sulphuryl chloride can then be distilled from the product. A. Fränkel described the preparation of sulphuryl chloride by a similar process. T. P. van der Goot measured the f.p. of mixtures of chlorine and sulphur dioxide, expressed as molar precentages, and found:

SO_2 .	0	0·7	3·0	9·6	24·1	54·6	70·9	91·4	100
F.p. .	−109·9°	−101·1°	−102·2°	−95·3°	−89·4°	−86·7°	−84·7°	−79·7°	−75·2°

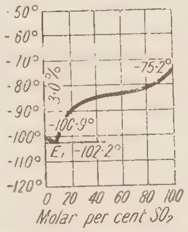


FIG. 145.—Freezing-point Curve of the System: Cl_2–SO_2 (without catalyst).

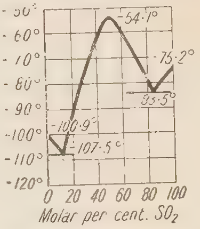


FIG. 146.—Freezing-point Curve of the System: Cl_2–SO_2 (with catalyst).

These data, plotted in Fig. 145, show that no chemical combination occurs; if, however, a trace of camphor be present, the curve, Fig. 146, is obtained, where the maximum at −54·1° corresponds with the formation of sulphuryl chloride, SO_2Cl_2. The eutectic, E_1, at −107·5° corresponds with 15·3 molar per cent. of SO_2, and that at

—83·5° with about 85 per cent. SO_2. A. Smits and W. J. de Mooy found —102·3° for the eutectic temp. with 1·9 molar per cent. of sulphur dioxide.

According to H. Schulze, camphor readily absorbs sulphur dioxide and thereby liquefies, and the absorbed gas escapes when the liquid is exposed to air. Chlorine gas has no action on camphor, but it is greedily absorbed by the above liquid until saturated, and a soln. of camphor in sulphuryl chloride is formed, which can be easily separated and obtained pure by distillation. This action cannot be due to the mere condensation of the sulphurous anhydride and its action in the liquid state on the chlorine, for these two gases do not combine even when condensed and cooled to −20°; but, on the other hand, in presence of camphor the reaction takes place even at −20°. Sulphurous anhydride combines in large proportion with and liquefies glacial acetic and formic acids; these acids are scarcely attacked by chlorine if sunlight is excluded, but the sulphurous compounds greedily absorb chlorine with formation of sulphuryl chloride, the acetic and formic acids remaining almost unacted on; thus their mode of action seems to resemble that of camphor. Alcohol and acetone also absorb quantities of sulphur dioxide; chlorine passed through these liquids acts on the alcohol and acetone, and in proportion as this proceeds the sulphurous anhydride escapes without being acted on. Other absorbents of sulphurous anhydride are sulphuryl chloride itself, and liquid sulphur trioxide. Chlorine passed into the latter soln. does not yield a trace of sulphuryl chloride, no more than it does with the former. Turpentine absorbs sulphur dioxide, but it does not effect the union of this body with chlorine. Carbon bisulphide and chloroform absorb chlorine, but the soln. is not acted on by sulphur dioxide. It cannot be supposed that the action of camphor, or acetic or formic acids, is due to their combining momentarily with chlorine, and then passing it over to the sulphur dioxide *in statu nascendi*, for the first two undergo substitution to a slight extent only and the last is completely decomposed into carbonic anhydride and hydrochloric acid. If chlorine is passed into a soln. of sulphur dioxide in camphor, but not to saturation, and the bulk of the sulphuryl chloride is then removed by distillation and the rest by shaking repeatedly with water, there remains pure camphor containing no trace of chlorine substitution-products. But if chlorine is passed to saturation, substitution-products are formed, and increase in quantity on standing and introduction of more chlorine; at 0°, however, this action is extremely slow. The solvent power of the sulphuryl chloride formed doubtless helps the action of the camphor; but this dilution of the camphor, most favourable at 1 : 50, stops the reaction at 1 : 100. A mixture of the two gases has naturally the same effect as above, but not until about two parts of sulphuryl chloride are formed to one of camphor does the reaction go on rapidly. With glacial acetic acid, the preparation may be carried on just as easily, but with formic acid, when about five times its volume of sulphuryl chloride is formed, the liquid separates into two layers, the upper one consisting of the formic acid containing some sulphuryl chloride.

G. Cusmano said that the life of the catalyst employed in the reaction $SO_2+Cl_2=SO_2Cl_2$ depends on its resistance to chlorination by chlorine or sulphuryl chloride; he found that ketocineole, *cyclo*hexanone, menthone, and tetrahydrocarvone act like camphor in accelerating the reaction $SO_2+Cl_2=SO_2Cl_2$, but not so with α-bromocamphor, camphorsulphonic acid, camphorquinone, or monobromo- or monochloro-ketocineole—the reaction is, however, accelerated by introducing a positive radicle into these compounds, thus, when ammonium chloride, and nitrogen heated together with iron at 300° under 50 atm. press.: $3Fe+6NH_4Cl+2N_2=3FeCl_2+8NH_3$. A gaseous mixture is obtained containing up to 99 per cent. of ammonia. The portion of this derived from the ammonium chloride may be allowed to react with the ferrous chloride; the ferrous hydroxide formed is reduced and the ammonium chloride recovered for further use.

T. H. Durrans, and A. B. Roberts and T. H. Durrans found that the following substances catalyzed the reaction well: Ethyl acetate, ethyl *iso*butyrate, ethyl acetoacetate, ethyl phenylacetate, ethyl benzoate, ethyl cinnamate, ethyl malonate, *iso*amyl formate, *iso*amyl acetate, *iso*amyl nitrate, benzyl acetate, benzyl benzoate, benzyl cyanide, phenyl acetate, glyceryl triacetate, dichlorohydrin, phenyl phosphate, *o*-cresyl phosphate, ethyl ether, benzyl ether, amyl methylal, *p*-tolyl methyl ether, eucalyptole, methyl-*iso*eugenol, benzaldehyde, anisaldehyde, acetylacetone, *cyclo*hexanone, acetophenone, α-pinene, limonene. Of more moderate activity are: Acetal, *iso*butyl chloride, benzophenone, carvone, acetone, pyridine; whilst those found to be inactive or nearly so comprise: methyl benzoate, *iso*amyl benzoate, methyl monochloroacetate, *n*-butyl trichloroacetate, methyl sulphate, glycerol, benzoic acid, oleic acid, *n*-butyric acid, monochloroacetic acid, trichloroacetic acid, cinnamic acid, salicylic acid, phenylacetic acid, pentane, benzene, toluene, nitrobenzene, benzoyl chloride, acetyl chloride, chloroform, carbon tetrachloride. The following substances on treatment with the gas mixture reacted: anisole, anethole, estragole, citral, acetaldehyde, salicylaldehyde, cinnamaldehyde, methyl, ethyl, *n*-butyl, *iso*butyl, and benzyl alcohols, menthol, *iso*eugenol, and naphthalene.

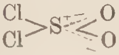
T. H. Durrans added that acids, with the exception of acetic acid, appear to have little or no catalytic action, and acetic acid itself is but a poor catalyst, whereas esters are good catalysts and the salts of acids react with sulphuryl chloride. Curious exceptions among the esters are those of the chloroacetic and sulphuric acids, which are quite inactive, whereas the esters of phosphoric and nitric acids are good catalysts. There seem to be no obvious common characteristic among the substances which catalyze the reaction to which this action can be ascribed ; nor does the degree of solubility of the mixed gases seem to have more than a secondary hearing. This point is further borne out by the fact that if a large volume of sulphuryl chloride be taken and to it be added a small quantity of one of the non-catalysts no acceleration of the absorption can be noticed, this being very slow, but if a similar quantity of a good catalyst be added the effect is quite decided. The use of one or other of the gases in an excess over the equimolecular proportion will cause a progressive slackening of the reaction, but on correctly proportioning the gases in the soln., the formation of sulphuryl chloride will ultimately proceed smoothly, provided that the catalyst is itself not permanently changed. If actual chemical reaction has taken place between one of the gas components and the catalyst, the former rate of absorption cannot be attained and the reaction may cease entirely. It is inferred that only substances possessing residual affinity in some form are capable of catalyzing this reaction, and that they exert this function by forming simultaneously with both chlorine and sulphur dioxide loose compounds, which then proceed to interact to form sulphuryl chloride and to regenerate the free catalyst. The final reaction, being bimolecular, would have the greatest velocity when the concentrations of the two loose compounds were equal—this, in fact, being the case. Furthermore, an excess of one of the gases tends progressively to saturate the catalyst at the expense of the other gas, thus inhibiting the final reaction by upsetting the equimolecular ratio.

M. Trautz found the order of the reaction in the presence of a little animal charcoal is more nearly normal with the decomposition than with the formation. In the latter case the velocity constant decreases rapidly towards the end of the reaction. The formation of sulphuryl chloride in glass vessels under the influence of light from a quartz mercury lamp is of the second order at 99°, and gives a good constant. The photochemical reaction does not, however, lead to sulphuryl chloride alone, but many other substances are formed, which cause the velocity constant to decrease. In the case of the decomposition, the presence of these other substances makes it impossible to calculate a velocity constant. An increase in temp. of 80° decreases the velocity of formation by an amount corresponding with a temp. coeff. of 0·88 per 10°. It was not possible to determine how far this is to be attributed to a shift in the position of equilibrium or to the disturbing influence of the secondary products ($S_2Cl_2,SO_3,SOCl_2,S_2O_5Cl_2,S_2O_3Cl_4$). The velocity of formation of sulphuryl chloride by light is of the same order as that in the presence of carbon in the dark, the effect being the same with a quartz mercury lamp and with a uviol lamp. M. le Blanc and co-workers found that in the system $SO_2+Cl_2\rightleftharpoons SO_2Cl_2$, the chlorine absorbs all light from the visible region to the middle ultra-violet and has a maximum at 340$\mu\mu$; sulphur dioxide has an absorption maximum at 290$\mu\mu$ and a minimum at 240$\mu\mu$; while sulphuryl chloride vapour absorbs all light from 300$\mu\mu$ upwards. The formation of secondary products in the reaction does not occur to the extent of 10 per cent. (i) When the system is illuminated by light which is almost wholly absorbed by sulphuryl chloride, the decomposition is quantitative between 55° and 100°, and the concentration has no perceptible influence on the course of the reaction. (ii) When the system is illuminated by light which is absorbed only by sulphur dioxide, only a slight reduction of press. occurs, and this is not due to the formation of sulphuryl chloride, but to a side reaction. (iii) When the system is illuminated by light which is absorbed only by chlorine, the formation of sulphuryl chloride continues until a stationary condition is set up. The velocity and also the position of the stationary condition depend, at constant temp., on the presence of a small quantity of water, and the higher the temp. the earlier the stationary condition is reached. In a number of cases a reversal is noted, so that the stationary condition does not come at the end of diminution of press., but of an increase in press. At the temp. 105° and 125°, at which the equilibrium in the dark is known, the stationary condition lies more to the side of sulphuryl chloride than in the non-illuminated reaction. The lower the temp. the further apart are the end-points of the illuminated and the non-illuminated reactions. The temp. coeff. of the formation of sulphuryl chloride from chlorine and sulphur dioxide by light which is only absorbed by chlorine is small, and has little influence on the course of the reaction. According to J. K. Syrkin, sulphuryl chloride decomposes at a higher speed than is accounted for by the radiation theory. H. Tramm studied the effect of moisture on the photochemical formation of sulphuryl chloride.

A. Besson and L. Fournier observed that a little sulphuryl chloride is formed when sulphur dioxide acts on sulphur monochloride at 160°–170°. A. W. Williamson said that when phosphorus pentachloride acts on conc. sulphuric acid, chlorosulphonic acid is first formed and then sulphuryl chloride. C. Gerhardt and L. Chiozza said that phosphoryl chloride and sulphur trioxide are formed. H. Schiff, and A. W. Williamson also said that it is produced by the action of phosphorus pentachloride on sulphur trioxide, but A. Michaelis did not agree, and he also said that it is not formed by the action of phosphoryl chloride on pyrosulphuryl chloride. L. Carius said that sulphuryl chloride is formed by the action of phosphorus pentachloride or of phosphoryl chloride on sulphates —*e.g.* lead sulphate—but A. Michaelis could not confirm this. L. Carius said that sulphuryl chloride is formed by the action of phosphorus pentachloride on benzolsulphonic acid, and by the action of sulphur chloride on sulphates ; and G. Gustavson, by the action of boron trichloride on sulphur trioxide.

A. W. Williamson said that chlorosulphonic acid yields small quantities of sulphuryl chloride on repeated distillation, but P. Behrend could not verify this ; however, he did find that when chlorosulphonic acid is heated for 12 hrs. to 170°–180° in sealed tubes, it is completely converted into sulphuric acid and sulphuryl chloride, $HO.SO_2.Cl=(HO)_2SO_2+Cl_2SO_2$. The contents of the tube were repeatedly distilled at 110°. The product was mixed in a separatory funnel with acid water ; the chlorosulphonic acid is decomposed, while the sulphuryl chloride is scarcely attacked, and collects as an oily liquid at the bottom. It is dried over phosphorus pentoxide, and then distilled over a water-bath. H. Beckurts and R. Otto said that the yield by P. Behrend's process is small, and they found sulphur dioxide and chlorine among the products of the reaction since sulphuryl chloride even at 230°–250° does not give these products. The action is therefore represented : $2(HO)SO_2Cl—Cl_2+HO.SO_2.SO_2.OH$, and $HO.SO_2.SO_2.OH=SO_2+H_2SO_4$. O. Ruff found that the reaction is reversible : $2Cl(HSO_3)\rightleftharpoons SO_2Cl_2+H_2SO_4$. A. Wohl and O. Ruff observed that the transformation of chlorosulphonic acid into molecular proportions of sulphuric acid and sulphuryl chloride is readily effected by boiling the compound with mercury or mercuric sulphate. If the apparatus is fitted with a reflux condenser at 70°, the sulphuryl chloride distils over in quantitative yield. The process is continuous, and other metallic salts, such as those of tin and antimony, may be employed as catalysts ; sulphur dichloride and iodine monochloride also produce the same effect. This process was recommended by L. Bert.

Sulphuryl chloride was described by H. V. Regnault, and P. Behrend as a colourless liquid, which fumes a little in air and possess a very penetrating odour. K. Heumann and P. Köchlin, and H. V. Regnault, P. Behrend, and B. von Pawlewsky found that the **vapour density** is normal for SO_2Cl_2 up to about 160°, and thereafter gradually decreases until at 440° dissociation is complete. M. Trautz, however, found that a marked dissociation occurs at a much lower temp. than this—*vide supra*. The vap. density at 157·66° and 738·5 mm. is 2·4129 in agreement with a 93·02 per cent. dissociation ; at 198·15° and 725·7 mm., 2·3749 and a 96·11 per cent. dissociation ; and at 256·82° and 732·4 mm., 2·3386 and a 99·16 per cent. dissociation. G. Oddo and E. Serra, and G. L. Ciamician found that the effect on the f.p. of benzene agrees with the **molecular weight** of SO_2Cl_2. G. Oddo obtained for the mol. wt. of soln. 0·527 and 2·454 grms. of sulphuryl chloride in 100 grms. of phosphoryl chloride respectively 179 and 145 —theoretical 135—by the f.p. process ; and G. Oddo and A. Casalino, for 1·9759 and 5·5435 grms. of sulphuryl chloride in 100 grms. of the complex $SO_3.2POCl_3$, 107·2 and 106·2 respectively. E. B. R. Prideaux represented the electronic structure:

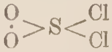


$$\begin{matrix}Cl\\Cl\end{matrix}>\overset{+}{S}<\begin{matrix}O\\O\end{matrix}$$

A. F. O. Getman discussed sulphuryl chloride as a solvent. H. V. Regnault gave for the **specific gravity** of the liquid 1·659 at 20°; P. Behrend, 1·661 at 21°; B. von Pawlewsky, 1·66738 at 20°/4°; R. Nasini and T. Costa, 1·685 at 12·4°/4°; and T. E. Thorpe, 1·70814 at 0°, and 1·56025 at the b.p., 69·95°; S. Sugden and co-workers gave for the sp. gr. 1·700 at 12°/4°, 1·671 at 25°/4°, and 1·640 at 38·5°/4°, or at θ°/4°, sp. gr.$=1{\cdot}727+0{\cdot}00227\theta$. T. E. Thorpe calculated that the **molecular volume** at the b.p. is 86·29. S. Sugden, and E. Rabinowitsch studied the mol. vol. W. Ramsay and J. Shields obtained 29·61 dynes per cm. for the **surface tension** at respectively 15·9° and 46·3°, and $a^2=3{\cdot}51$ sq. mm. for the **specific cohesion** at 15·9° and 3·14 at 46·3°. They also gave 540·9 ergs, and 475·2 ergs for the mol. **surface energy** at 15·9° and 46·3 respectively. N. von Kolossowsky studied the relation between the capillary constants and the heat of vaporization. T. E. Thorpe found that the **thermal expansion** is such that unit vol. at 0° becomes, at θ°, $v=1+0{\cdot}00123065\theta+0{\cdot}0_6759375\theta^2+0{\cdot}0_714578\theta^3$. M. Trautz gave −46° for the **freezing point** of the liquid; and T. P. van der Goot, −54·1°; H. V. Regnault gave 77° for the **boiling point**, but this datum is much too high; S. Sugden and co-workers gave 70·0° to 70·2° at 772 mm.; P. Behrend, 70·5°; G. Gustavson, 70°–71°; F. Clausnizer, 72°–73°; J. Ogier, 69·9°; B. von Pawlewsky, 69·1°–69·2° at 760 mm., and 68·3° at 740 mm.; P. Walden, 68° at 745 mm., and 69·6° at 771 mm.; while J. Thomsen gave 70° at 765 mm. M. Trautz obtained for the **vapour pressure**, p mm., $p=0{\cdot}2$ mm. at −78°:

	0°	17·99°	34·73°	44·75°	49·96°	54·97°	59·62°	64·94°	68·71°
p .	40·92	95·2	209·6	314·8	385·6	463·4	546·4	656·2	744·7

The dissociation of the vapour prevented B. von Pawlewsky measuring the **critical temperature.** M. Trautz found the **heat of vaporization,** λ, to be 6·829 Cals. per mol. at 64·02°; 6·178 Cals. at 64·52°; 6·683 Cals. at 69·13°; and 6·667 Cals. at 69·2°; and he gave $\lambda=(1-0{\cdot}01818p)(8940+3{\cdot}5T-0{\cdot}02845T^2)$, where p denotes the vap. press. in mm. at the absolute temp. T°. J. Ogier gave 524 cals. per gram for the heat of vaporization, and 0·233 for the **specific heat** of the liquid between 15° and 63°. M. Trautz gave 0·112 for the sp. ht. of the vapour between 16° and 99°; and for the **molecular heat,** $C_p=15{\cdot}5$. E. Beckmann studied the use of sulphuryl chloride as an ebulliscopic solvent. J. Ogier gave for the **heat of formation** $(S,O_2,Cl_2)=82{\cdot}54$ Cals.; and J. C. Thomlinson found that the calculated heat of formation of 87·948 Cals., agrees best with the assumption that the sulphur is sexivalent $O_2\equiv S=Cl_2$. M. Trautz gave for the heat of formation $(SO_2,Cl_2)=18{\cdot}696$ Cals., 7·55 Cals. for the heat of liquefaction at 17·84°; and hence, at 0°, the heat of formation is 10·304 Cals. per mol. The calculated **chemical constant** is 3·32. J. Thomsen found for the decomposition of sulphuryl chloride by water, $(SO_2Cl_2,Aq.)=62{\cdot}904$ at 17·839°. D. F. Smith calculated the thermal value of the reaction to be 46·4 Cals. between 289·3° and 299·5°; 51·85 Cals. between 299·5° and 320·1°; and 55·7 Cals. between 320·1° and 339·4°. R. Nasini and T. Costa gave for the **index of refraction** 1·458, 1·452, and 1·443 respectively with the H_γ-ray, the F-ray, and the C-ray at 12·4°. B. von Pawlewsky gave 1·44372 for the D-ray at 20°, and 35·92 for the molecular refraction, when the value calculated for quadrivalent sulphur in the formula



$$\begin{matrix}O\\\dot{O}\end{matrix}>S<\begin{matrix}Cl\\Cl\end{matrix}$$

is 35·76–35·89. M. le Blanc and co-workers found that the **absorption spectrum** of sulphuryl chloride vapour extends from 300$\mu\mu$ upwards. P. Walden found sulphuryl chloride to be an ionizing solvent; and he gave 8·5 for the **dielectric constant** at 20°; and H. Schlundt, 9·15 at 22°.

H. V. Regnault observed that sulphuryl chloride is decomposed by **water** into hydrochloric and sulphuric acids with the evolution of much heat; a little moisture was stated by W. Odling to transform it into chlorosulphonic acid. G. Carrara and I. Zoppellari observed that in this non-homogeneous system, the reaction is of the first order, and obeys the same laws as actions of the same order in a homogeneous system. The velocity of the reaction is the same when $0\cdot1N$-KOH is used instead of water, thus showing that the sulphuryl chloride is decomposed by the water and not by the alkali-lye. A. von Bäyer and V. Villiger said that the *monohydrate*, $SO_2Cl_2.H_2O$, is produced on adding sulphuryl chloride to ice-cold water; the substance resembles camphor in appearance and melts at the ordinary temp. It is only slightly soluble in cold water, and is but slowly decomposed by this solvent at 0°; on allowing the temp. of the mixture to rise, the crystals disappear and the original chloride is regenerated, the inverse change taking place when the reagents are cooled. The hydrate is stable even in the presence of sodium hydrocarbonate, and the formation of the crystals is observed on adding sulphuryl chloride to an ice-clad aq. soln. of this alkali. The stability of the hydrate towards water and the hydrocarbonate seems to indicate that the elements of water are not added to the acid chloride in such a manner as to form the dihydroxide, $SOCl_2(OH)_2$, for such a substance has a constitution corresponding with chlorosulphonic acid, $SOCl(OH)$, a compound instantly decomposed in aq. soln. G. Carrara has criticised these observations. A. Michaelis found that the first product of the action of a little water on sulphuryl chloride is chlorosulphonic acid: $SO_2Cl_2+H_2O=HCl+HO.SO_2.Cl$. According to R. H. McKee and C. M. Salls, in cases where the surplus chlorine of an electrolytic plant is given off as hydrochloric acid, it is economical to convert it to sulphuryl chloride, and decompose the latter where the acid is required. The reaction is carried out in a packed tower with steam and sulphuryl chloride in the vapour phase, and dil. sulphuric acid as liquid. The heat of the reaction is 67 cals. per mol SO_2Cl_2. T. P. van der Goot obtained for the f.p. of mixtures of **chlorine** and sulphuryl chloride, expressed as molar percentages:

SO_2Cl_2 .	0	3·3	**22·7**	30·5	64·0	84·5	91·2	100
F.p. .	−100·9°	−102·1°	**−109·1°**	−100·4°	−74·2°	−61·4°	−58·4°	−54·1°

The results are plotted in Fig. 147. The eutectic, E_2, is at −109·1° and 22·7 molar per cent. SO_2. There is no sign of a higher chloride. M. Trautz observed that **bromine** and **iodine** exerted no catalytic action on the decomposition of sulphuryl chloride at 99·3°; and O. Ruff found that sulphuryl chloride does not react with iodine alone, but it does so in the presence of aluminium chloride or iodide, forming iodine monochloride: $SO_2Cl_2+I_2=2ICl+SO_2$, and the trichloride when the sulphuryl chloride is in considerable excess: $3SO_2Cl_2+I_2=2ICl_3+3SO_2$. A. Besson observed that dry **hydrogen bromide** at ordinary temp., or when gently heated, decomposed sulphuryl chloride, forming bromine, hydrogen chloride, and sulphur dioxide; **hydrogen iodide** behaves similarly, but some sulphur is liberated and water formed. M. Trautz observed no reaction with **calcium hypochlorite** at 99·3°.

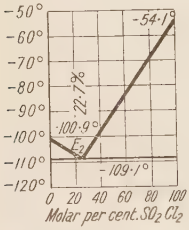


Fig. 147.—Freezing-point Curve of the System: Cl_2–SO_2Cl_2.

M. Trautz showed that **sulphur** does not exert any catalytic action on the decomposition of sulphuryl chloride at 99·3°; K. Heumann and P. Köchlin observed no chemical action; and O. Ruff found that sulphur crystallizes unchanged from sulphuryl chloride when the two substances are heated together at 130° and subsequently allowed to cool. H. B. North and J. C. Thomson found that at temp. from 75°–85°, the sulphuryl chloride dissolved and crystallized on cooling; between 95°–98°, about one-fifth of the sulphur separated on cooling; and none after heating to 125°; and the reaction $SO_2Cl_2+2S=S_2Cl_2+SO_2$ appeared to be complete.

According to O. Ruff, the chlorination of sulphur by sulphuryl chloride occurs only when the temp. attains 200°, but if aluminium chloride be present, the reaction $SO_2Cl_2+2S=S_2Cl_2+SO_2$ is quantitative between 30° and 70° ; with less sulphur, the reaction $SO_2Cl_2+S=SCl_2+SO_2$ is quantitative at 40°. No thionyl chloride was formed under these conditions. The effect of the aluminium chloride is attributed to the formation of *aluminium sulphurylchloride*, $AlCl_3.SO_2$, as an intermediate compound $AlCl_3+SO_2Cl_2\rightleftharpoons AlCl_3.SO_2+Cl_2$. This is confirmed by the fact that whilst a current of dry carbon dioxide passed through a flask containing sulphuryl chloride carries sulphur dioxide and chlorine with it in eq. proportions, there is an excess of chlorine evolved when aluminium chloride has been added to the sulphuryl chloride ; further, if the temp. be gradually raised to 120°, the residue in the flask is largely $AlCl_3.SO_2$. It is assumed that the reaction is reversible, but it was not possible to obtain a satisfactory equilibrium constant owing to another reaction, namely : $AlCl_3.SO_2\rightleftharpoons AlCl_3+SO_2$. The compound $AlCl_3.SO_2$ is stable at 100° in an atm. of sulphur dioxide, but in sulphuryl chloride soln. it can be entirely decomposed at the ordinary temp. by carrying off the free sulphur dioxide with a current of dry carbon dioxide. The net result, therefore, of adding aluminium chloride to sulphuryl chloride is the simultaneous production of sulphur dioxide, chlorine, and the double compound $AlCl_3,SO_2$, in other words, aluminium chloride increases the extent to which sulphuryl chloride is dissociated. The chlorine liberated in the reaction between aluminium chloride and sulphuryl chlorides converts sulphur into sulphur monochloride ; and the aluminium chloride is regenerated by $AlCl_3.SO_2\rightleftharpoons AlCl_3+SO_2$. Unlike many other catalytic reactions, the aluminium chloride is here involved in the equilibrium akin to the *Pseudokatalyse* of J. Wagner, or the *Uebertragungskatalyse* of W. Ostwald ; and when the catalytic agent increases the dissociation of one of the reacting substances, as here, O. Ruff proposed the term *Dissociationskatalyse*. P. Rohland also discussed the catalytic reactions produced by aluminium chloride. A. Besson said that **hydrogen sulphide** acts on sulphuryl chloride in the cold, forming sulphur, sulphur dioxide, and hydrogen chloride: $SO_2Cl_2+H_2S=2HCl+SO_2+S$, but some sulphur monochloride is formed in a proportion which increases as the temp. rises ; some water is produced at the same time : $SO_2Cl_2+2H_2S=2H_2O+S_2Cl_2+S$. T. P. van der Goot found for the f.p. of mixtures of **sulphur dioxide** and sulphuryl chloride, expressed in molar percentages :

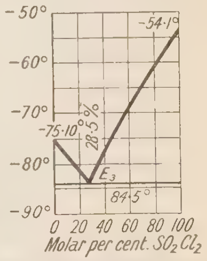


FIG. 148.—Freezing-point Curve of the System : SO_2–SO_2Cl_2.

SO_2Cl_2 .	0	5·5	28·5	33·0	53·4	64·8	93·1	100
F.p. .	−75·1°	−77·4°	−84·5°	−83·7°	−74·3°	−69·5°	−57·4°	−54·1°

The results are plotted in Fig. 148. There is here no evidence of chemical combination. The eutectic, E_3, is at −84·5° and 28·5 molar per cent. SO_2Cl_2. For the ternary system : SO_2Cl_2–Cl_2–SO_2, Fig. 149, there is no evidence of any compound other than sulphuryl chloride. The ternary eutectic, *E*, is at −111·6°, and 76 per cent. of chlorine, 16 per cent. of sulphuryl chloride, and 8 per cent. of sulphur dioxide. A. Michaelis represented the reaction with conc. **sulphuric acid :** $SO_2Cl_2+H_2SO_4=2Cl(HSO_3)$. V. Lenher found that **selenium** is rapidly attacked by sulphuryl chloride with the development of heat and the formation of selenium tetrachloride and sulphur dioxide ; no reaction was observed with **selenium dioxide** at a high temp. or high press. F. Clausnizer said that sulphuryl chloride reacts with **selenium tetrachloride,** forming $Cl.SO_2.O.SeCl_3$ (*q.v.*), and with **selenium dioxydichloride,** at 170°–180°, in a sealed tube : $SO_2Cl_2+SeOCl_2$

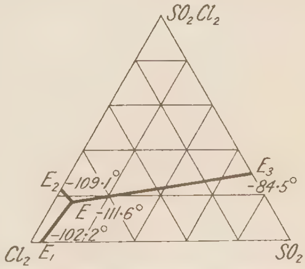


FIG. 149.—Freezing Points of the Ternary System : SO_2Cl_2–Cl_2–SO_2.

$=SO_3.SeCl_4$. B. von Horvath found that at ordinary temp., **tellurium** reacts with sulphuryl chloride in an atm. of carbon dioxide at a red-heat, forming tellurium tetrachloride and sulphur dioxide. V. Lenher observed that when sulphuryl chloride acts on tellurium in a sealed tube tellurium dichloride and afterwards the tetrachloride is formed; and when the vapour of sulphuryl chloride is passed over **tellurium dioxide** there is no reaction.

According to H. V. Regnault, sulphuryl chloride reacts with gaseous **ammonia**, forming ammonium chloride and sulphuryl amide. W. Traube saturated with dry ammonia a soln. of sulphuryl chloride in 15–20 times its vol. of chloroform, and obtained what appeared to be sulphuryl amide and imide (*q.v.*). A. Hantzsch and co-workers obtained trisulphimide: $3SO_2Cl_2+12NH_3=6NH_4Cl+(SO_2:N.NH_4)_3$; and F. Ephraim and F. Michel, and M. Gurewitsch, found imidosulphamide (*q.v.*) to be the chief product. The action of **hydrazine** compounds on sulphuryl chloride was discussed by F. Ephraim and E. Lasocky—*vide* the sulphohydrazides. W. C. Williams found that sulphuryl chloride is inert towards **nitric acid**; and he represented the reaction with **potassium nitrate**: $SO_2Cl_2+2KNO_3=N_2O_4+Cl_2+K_2SO_4$, but the reaction takes place with difficulty and is incomplete. T. E. Thorpe observed no reaction with **silver nitrate.** A. Mente found that when **ammonium carbamate** acts on sulphuryl chloride, ammonium imidosulphonate, and ammonium chloride are formed. M. Trautz found red and yellow **phosphorus** have scarcely any action on sulphuryl chloride at 99·3°; K. Heumann and P. Köchlin found that there is only a feeble reaction with yellow phosphorus, but the reaction is more energetic with red phosphorus, and sulphur dioxide and phosphorus trichloride are formed. H. B. North and J. C. Thomson found that the reaction with white or red phosphorus at 120° may be represented $3SO_2Cl_2+2P=2PCl_3+3SO_2$, at a higher temp. and with an excess of sulphuryl chloride some phosphorus pentachloride is formed: $PCl_3+SO_2Cl_2=PCl_5+SO_2$, but this reaction is far from complete. A. Besson found that **phosphine** reacts with sulphuryl chloride, forming hydrogen chloride, phosphorus tritetritasulphide, red phosphorus, and traces of phosphorus trioxide and phosphoryl chloride. M. Trautz said that **phosphorus trichloride and pentachloride** are *so gut wie wirkunglos* at 99·3°, while A. Michaelis observed that phosphorus pentachloride gradually decomposes sulphuryl chloride, forming thionyl chloride, phosphoryl chloride, and chlorine. D. Balareff said that boiling sulphuryl chloride converts **orthophosphoric** acid into the pyro-acid. K. Heumann and P. Köchlin found that **arsenic** reacts with heated sulphuryl chloride, forming a mixture of arsenic trioxide and trichloride; and **antimony** forms antimony trichloride. M. Trautz observed no reaction with antimony at 99·3°. E. Beckmann found that **arsenic trioxide** is not dissolved by boiling sulphuryl chloride. F. Clausnizer observed that sulphuryl chloride has no action on **antimony trichloride.** O. Ruff observed that **antimony trisulphide** dissolves in sulphuryl chloride, forming antimony trichloride with the separation of sulphur, but in the presence of aluminium chloride, sulphur dichloride is produced. F. E. Brown and J. E. Snyder found that **vanadium oxytrichloride** is miscible in all proportions with sulphuryl chloride.

K. Heumann and P. Köchlin found that **carbon** has no action on sulphuryl chloride, and M. Trautz observed that while ordinary wood charcoal has very little action at 100°, prepared animal charcoal accelerates the attainment of the equilibrium $SO_2Cl_2\rightleftharpoons SO_2+Cl_2$, catalytically. K. Heumann and P. Köchlin showed that sulphuryl chloride acts on **organic acids** like phosphorus tri- and penta-chloride, exchanging the hydroxyl group for chlorine—thus, with sodium benzoate, benzoic chloride and anhydride are produced. Analogous reactions were observed by M. Conrad and H. Reinbach, A. Peratoner, H. Kast, A. Dubois, and W. R. Smyth. Mercury, camphor, and iodine have been used as catalytic agents in these reactions. W. Foster said that when **ethylene** is bubbled through sulphuryl chloride, no apparent change occurs; but by varying the conditions, ethylene dichloride and sulphur dioxide are formed. A. Dubois chlorinated benzene by heating it with sulphuryl chloride in a sealed tube at 150°; A. Töhl and O. Eberhard found that a temp.

of 160°–170° was necessary. O. Silberrad found that with aluminium chloride as catalyst, the chlorination of benzene occurs in a few minutes at ordinary temp. He also examined the effect of iodine, sulphur, thionyl chloride, sulphur monochloride, and ferric chloride as catalytic agents; the best results were obtained with a mixture of a soln. of sulphur monochloride in sulphuryl chloride along with aluminium chloride. A. Töhl and O. Eberhard chlorinated **hydrocarbons** –*e.g.* toluene, *m*-xylene, *p*-xylene, mesitylene, pseudocumene, durene, prehnitine, pentamethylbenzene, ethylbenzene, *iso*propylbenzene, and cymene—with sulphuryl chloride. A. Dubois obtained chlorobenzene from **benzene** and sulphuryl chloride at 16°; and O. and C. A. Silberrad and B. Parke studied the effect of various catalysts on the chlorination of **toluene.** P. Behrend studied the action of sulphuryl chloride on various **alcohols**—methyl, ethyl, isobutyl, and benzyl—and found that the corresponding chlorosulphonate is formed: $SO_2Cl_2+CH_3OH=HCl+Cl.SO_2.OCH_3$. R. Levaillant and L. J. Simon showed that the reaction with methyl alcohol probably occurs in two stages: $SO_2Cl_2+CH_3OH=CH_3O.SO_2.Cl+HCl$ and $CH_3O.SO_2.Cl+CH_3OH=(CH_3)_2SO_4+HCl$. F. W. Bushong studied the action of sulphuryl chloride on sodium alcoholates. H. Danneel discussed the properties of soln. of paraldehyde and metaldehyde in sulphuryl chloride; K. G. Naik and M. L. Shah, the action of sulphuryl chloride on substances containing methylene. L. Wenghöffer, and W. Eller and L. Klemm, chlorinated **aromatic amines** –*e.g.* aniline—by sulphuryl chloride; and K. Fuchs and E. Klatscher, α-trioxymethylene; B. Holmberg represented the reaction with **mercaptans,** $2C_2H_5.SH+SO_2Cl_2=(C_2H_5)_2S_2+SO_2+2HCl$. The reaction was studied by H. S. Tasker and H. O. Owen. A. Wohl chlorinated acetic acid by heating it with sulphuryl chloride at 115°–120° under 4 to 5 atm. press. U. Colacicchi studied the action of sulphuryl chloride on *s*-dimethylpyrrole; B. Oddo, and E. Cherbuliez and O. Schnauder on organomagnesium compounds; T. H. Durrans, on monosubstituted benzenes.

M. Trautz observed that **silicon** has no action on sulphuryl chloride at 99·3°. F. Clausnizer observed that sulphuryl chloride does not react with **silicon tetrachloride.** K. Heumann and P. Köchlin found that sulphuryl chloride does not attack **sodium** vigorously. E. Fromm said that a soln. of sulphuryl chloride in absolute ether does not act on sodium or on powdered **copper.** H. B. North found that **silver** does not react with sulphuryl chloride even at 300°; **gold** is attacked after a prolonged heating in a sealed tube at 150°, forming anhydrous auric chloride. E. Fromm found that an ethereal soln. of sulphuryl chloride does not act on **magnesium.** H. B. North said that **zinc,** and **cadmium** do not react at 300°; but E. Fromm and J. de Seixas-Palma represented the action of a dry ethereal soln. of sulphuryl chloride on zinc-dust in the cold by $SO_2Cl_2+2Zn=ZnCl_2+ZnSO_2$—zinc sulphoxylate—and $Zn+SO_2Cl_2=ZnCl_2+SO_2$. H. B. North found that **mercury** reacts $Hg+SO_2Cl_2=HgCl_2+SO_2$ at 160°–180°, and with an excess of mercury, the solid product is mainly mercurous chloride; and at 99·3°, M. Trautz observed that mercury and **aluminium** powder have no effect on sulphuryl chloride. K. Heumann and P. Köchlin found that **tin** is not strongly attacked by sulphuryl chloride. M. Trautz observed that **vanadium, molybdenum,** and **tungsten** have no effect on sulphuryl chloride at 99·3°; and a similar result was obtained with powdered **iron.** E. Fromm observed that an ethereal soln. of sulphuryl chloride does not act on powdered iron. R. H. McKee and C. M. Salls found that iron is not attacked at ordinary temp. H. B. North found that iron behaves like gold, forming anhydrous ferric chloride; and similarly with **platinum,** which forms anhydrous platinic chloride; M. Trautz observed that **palladium** black has no action on sulphuryl chloride at 99·3°.

E. Spelta said that sulphuryl chloride is readily formed from chlorine and sulphur dioxide and is readily decomposed into these components. The chlorinating action of sulphuryl chloride is attributed to a slightly stable linking between the sulphur dioxide and chlorine. This linking must have a special form since rupture occurs preferably in the presence of elements having an electropositive character.

I. Guareschi found that sulphuryl chloride is absorbed by **soda-lime.** Sulphuryl chloride does not react with **mercuric oxide** prepared in the dry way, but yellow mercuric oxide readily reacts with sulphuryl chloride in a sealed tube at 150° : $2HgO+SO_2Cl_2=HgSO_4+HgCl_2$; but if the sulphuryl chloride be in excess, some sulphur trioxide is formed : $HgO+SO_2Cl_2=HgCl_2+SO_3$. H. B. North found that red mercuric oxide behaves similarly at 160°–180°. Some mercurous chloride is also produced. E. Spelta observed no reaction between sulphuryl chloride and **lead oxide** heated in a sealed tube for several hours at 140°–150° ; the reaction with **lead dioxide** may take place with explosive violence : $2PbO_2+SO_2Cl_2=PbSO_4+PbCl_2+O_2$; if the sulphuryl chloride is in slight excess, the temp. may rise above its b.p. and chlorine may be formed. M. Trautz observed no reaction occurs with **cuprous chloride** at 99·3° ; E. Beckmann found that boiling sulphuryl chloride does not dissolve **molybdenum trioxide** or **tungsten trioxide.** M. Trautz observed that at 99·3° sulphuryl chloride has no action on **mercurous or mercuric chloride, aluminium chloride**—*vide supra*—**stannous chloride,** anhydrous **ferric chloride,** or **potassium dichromate.** F. Clausnizer observed no reaction between sulphuryl chloride and **stannic chloride.** O. Ruff said that **molybdenum pentachloride** readily dissolves in sulphuryl chloride to a brown soln., and is then readily reduced (by sulphur, for example) to the yellow dichloride ; on adding aluminium chloride, it is immediately rechlorinated with evolution of sulphur dioxide, and, on cooling, a double-compound of molybdenum pentachloride and sulphur chloride separates from the soln.

According to W. Odling,[3] **sulphuryl bromide,** SO_2Br_2, is produced, slowly and incompletely, when a mixture of bromine and dry sulphur dioxide is exposed to sunlight. The product was said to be a white, crystalline solid which, when heated with an excess of silver sulphate in a sealed tube, forms silver bromide and sulphur trioxide : $SO_2Br_2+Ag_2SO_4=2AgBr+2SO_3$. F. Sestini observed that liquid sulphur dioxide dissolves bromine, forming an orange-red liquid which does not change its colour in sunlight. Neither G. Gustavson, nor H. L. F. Melsens was able to confirm W. Odling's statements. M. Trautz said that sulphuryl bromide is not formed from sulphur dioxide and bromine at temp. between 106° and 202° ; or in light from a Nernst's lamp in the absence of catalysts. H. Schulze observed no formation of sulphuryl bromide from bromine and sulphur dioxide in the presence of camphor ; or when sulphuryl chloride is treated with hydrogen bromide : $2HBr+SO_2Cl_2=Br_2+SO_2+2HCl$. According to H. Danneel, if sulphuryl bromide really exists, it decomposes at 18° with the evolution of sulphur dioxide. T. P. van der Goot measured the f.p. of mixtures of bromine and sulphur dioxide, and, expressing the results in molar percentages, found :

Br_2	100	76·5	69·4	26·9	15·7	2·5	**1·0**	0·7	0
F.p.	−7·1°	−13·3°	−13·8°	−15·8°	−21·7°	−58·0°	**−75·5°**	−75·3°	−75·1°

The results are plotted in Fig. 150. The eutectic is at −75·5° and 1·0 molar per cent. of bromine. The same curve was obtained in darkness, in light, and in the presence of camphor as catalyst. The general form of the curve is like that with the Cl_2–SO_2-system, Figs. 145 and 146.

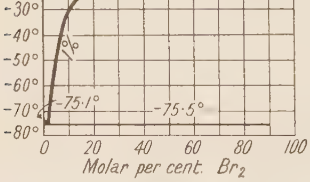


FIG. 150.—Freezing-point Curve of the System : SO_2–Br_2.

W. Odling said that when a mixture of iodine and dry sulphur dioxide is exposed to sunlight a compound corresponding with sulphuryl chloride is slowly formed—presumably **sulphuryl iodide,** SO_2I_2. F. Sestini found that liquid sulphur dioxide dissolves about one-seventieth part of iodine—approximately 1 c.c. dissolves 0·1 grm. of iodine—forming a brownish-red liquid which does not change in sunlight, and which furnishes crystals of iodine when cooled. H. Schulze observed no formation of sulphuryl iodide from sulphur dioxide and iodine in the presence of camphor, or when hydrogen iodide acts on sulphuryl chloride: $2HI+SO_2Cl_2=2HCl+I_2+SO_2$. There is therefore no reliable evidence establishing the individuality of sulphuryl bromide or iodide.

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§ 52. Sulphur Oxyhalides

H. Rose's observations,[1] mentioned in his paper: *Eine der Schwefelsäure entsprechende Chlorverbindung des Schwefels*, on the action of sulphur monochloride on sulphur trioxide have been previously discussed; he observed that **pyrosulphuryl chloride**, $S_2O_5Cl_2$, is a product of the reaction; and he regarded it as a compound of two mols. of sulphur trioxide in which an atom of bivalent oxygen is replaced by two atoms of univalent chlorine, $Cl.SO_2.O.SO_2.Cl$. He recommended the following mode of preparing this compound:

> Mix 20 to 30 vols. of fuming sulphuric acid, cooled by a freezing mixture, with one vol. of sulphur monochloride, saturated as much as possible with chlorine. The dark brown mixture on which a lighter liquid generally floats, is distilled. The excess of sulphur monochloride together with much sulphurous acid passes over first, and afterwards pyrosulphuryl chloride. Sulphuric acid remains in the retort. The distillate is freed from sulphuric acid by fractional distillation.

The reaction is presumably: $5SO_3+S_2Cl_2=S_2O_5Cl_2+5SO_2$. Sulphur trioxide may be chlorinated in other ways: A. Michaelis used thionyl chloride: $2SO_3+SOCl_2=S_2O_5Cl_2+SO_2$, phosphorus pentachloride: $2SO_3+PCl_5=S_2O_5Cl_2+POCl_3$, or phosphoryl chloride in a sealed tube at 160°: $6SO_3+2POCl_3=3S_2O_5Cl_2+P_2O_5$; H. E. Armstrong, chloroform: $2SO_3+CHCl_3=S_2O_5Cl_2+CO+HCl$; H. E. Armstrong, G. Oddo and A. Sconzo, G. Oddo, H. Erdmann, V. Grignard and P. Muret, and P. Schützenberger, carbon tetrachloride, $2SO_3+CCl_4=S_2O_5Cl_2+COCl_2$; M. Prud'homme, carbon hexachloride, $2SO_3+C_2Cl_6=S_2O_5Cl_2+C_2OCl_4$; G. Gustavson, silicon tetrachloride, $4SO_3+SiCl_4=2S_2O_5Cl_2+SiO_2$; and A. Rosenstiehl, sodium chloride, $4SO_3+2NaCl=S_2O_5Cl_2+Na_2S_2O_5$. Chlorosulphonic acid can be employed in place of sulphur trioxide, and A. Michaelis heated this substance with phosphorus pentachloride, $2ClHSO_3+PCl_5=S_2O_5Cl_2+POCl_3+2HCl$; and G. Billitz and K. Heumann, D. Konowaloff, and J. Ogier heated phosphorus pentoxide, and chlorosulphonic acid in a flask fitted with a reflux condenser: $2HClSO_3+P_2O_5=S_2O_5Cl_2+2HPO_3$, and obtained a 93 per cent. yield. C. Moureu heated 2 mols of sulphuric acid with 3 mols of thionyl chloride and obtained pyrosulphuryl chloride; A. Ditte heated sodium hydrosulphate or ferrous sulphate and sodium chloride; and H. Quantin, potassium or barium sulphate at a red-heat with carbon tetrachloride. W. Prandtl and P. Borinsky found this to be the most convenient process. A. Besson found that pyrosulphuryl chloride partially decomposes when boiled under ordinary press., but it can be fractionated under reduced press., and boils at 53° under a press. of 15 mm., whilst chlorosulphonic acid boils at 65° under the same press. It can be freed from chlorine by agitation with mercury, care being taken to keep the temp. well below 60°. Sulphur trioxide and chlorosulphonic acid are removed by adding phosphorus pentachloride in excess, and the pyrosulphuryl chloride is then readily purified by fractionation. Attempts to make pyrosulphuryl chloride by heating sulphuryl chloride and sulphur trioxide at 100°, or by prolonged exposure to sunlight, were not successful.

Pyrosulphuryl chloride is at ordinary temp. a colourless, mobile, refracting liquid. It fumes in air less than sulphur trioxide, and it has a peculiar odour quite distinct from that of sulphur dioxide. It was analyzed by H. Rose, A. Rosenstiehl, and H. E. Armstrong. H. Rose found the **vapour density** to be 4·329-4·586 ; J. Ogier, 3·73 to 3·74 ; A. Rosenstiehl, 3·76, and 5·66 at 202° ; W. Prandtl and P. Borinsky, 5·94 to 7·27 ; and D. Konowaloff, 7·3 when the calculated value for $S_2O_5Cl_2$ is 7·43. The high result was attributed by K. Heumann and P. Köchlin to the presence of sulphuric acid ; and the low results were attributed by D. Konowaloff to the presence of some chlorosulphonic acid ; but K. Heumann and P. Köchlin showed that the results between 160° and 442° depend on the temp. Near the b.p., the observed vapour density is near the theoretical value for $S_2O_5Cl_2$, but at 442°, the observed density is only half the theoretical value. H. Rose said that the vapour withstands a temp. of 217° without decomposition, but when passed through a red-hot tube it is partially resolved into chlorine and sulphurous and sulphuric oxides. The higher the temp. the greater the decomposition. H. E. Armstrong found evidence suggesting that a part of the sulphur trioxide unites with the excess of sulphuryl chloride, forming a liquid boiling below 100° and decomposing into its constituents in a current of carbon dioxide. According to A. Rosenstiehl, pyrosulphuryl chloride is completely decomposed at 200°, but not into sulphuryl chloride and sulphur trioxide as suggested by A. Lieben. The **specific gravity** was found by H. Rose to be 1·818 at 20° ; A. Michaelis gave 1·819 at 18° ; G. Carrara and I. Zoppelari, 1·8512 at 11°/4° ; V. Grignard and P. Muret, 1·834 at 19° ; A. Rosenstiehl, 1·762 ; and D. Konowaloff, 1·872 at 0°. W. Prandtl and P. Borinsky gave 1·876 at 0°, and 1·844 at 18°. T. E. Thorpe found 1·85846 at 0°, and 1·60610 at the b.p., 139·59° ; the molecular volume at the b.p. is 133·55 ; and the **thermal expansion** is such that the unit vol. at 0° becomes, at $\theta°$, $v=1+0·0009683\theta+0·0_6 86709\theta^2+0·0_7 18623\theta^3$. D. Konowaloff gave 0·249 for the **specific heat** between 18° and 80°, and 0·254 between 21° and 152° ; J. Ogier gave 0·258 between 15° and 130°. A. Besson found that when the purified liquid is strongly cooled, it forms a white, crystalline solid with the **melting point** —39°. H. Rose gave 145° for the **boiling point ;** A. Michaelis, 146° ; A. Rosenstiehl, 145°-150° ; H. E. Armstrong, 141°–145° ; P. Schützenberger, 130° ; D. Konowaloff, 153° at 752 mm. ; and T. E. Thorpe, 139·59° at 760 mm. ; J. Ogier, 140·5° ; and V. Grignard and P. Muret gave 57° at 30 mm., and 52° at 15 mm. The low results are referred by D. Konowaloff to the presence of chlorosulphonic acid ; and the high results, by K. Heumann and P. Köchlin to the presence of sulphuric acid. G. Billitz and K. Heumann gave 145°–147°, and A. Besson, 142°–143° at 765 mm. J. Ogier gave 68 cals. per gram, or 13·16 Cals. per mol for the **heat of vaporization** at 23·25°. According to J. Ogier, the **heat of formation** of liquid pyrosulphuryl chloride from its elements is 159·4 Cals. ; D. Konowaloff gave 188·2 Cals. ; J. Ogier found the heat of decomposition by water to be $S_2O_5Cl_2+H_2O=2ClHSO_{3liquid}+27$ Cals. ; and D. Konowaloff, for the heat of decomposition with potassium hydroxide soln. 0·896 Cal. per gram. V. Grignard and P. Muret gave 1·449 for the **index of refraction** at 19°. According to V. Grignard and P. Muret, the diamagnetism and mol. refraction indicate that sexivalent sulphur is present, and physical and chemical properties agree with the formula ClO.SO.O.SO.OCl.

V. Grignard and P. Muret said that pyrosulphuryl chloride is hygroscopic, and has a characteristic odour. They said that the vapour-density determinations at various temp. indicate that decomposition follows the irreversible equations, $S_2O_5Cl_2=SO_3+SO_2+Cl_2$ and $S_2O_5Cl_2=SO_3+SO_2Cl_2$, and this is confirmed by the analysis of the decomposition products. At 200°, in the presence of sulphur dioxide and chlorine, the first reaction occurs to a small extent, and gives place to the second reaction above this temp. The reaction $SO_2Cl_2\rightleftharpoons SO_2+Cl_2$ then occurs, and decomposition is complete at 360°. According to H. Rose, when pyrosulphuryl chloride is put into **water** it sinks to the bottom in oily drops which do not dissolve for several hours even when stirred. It appears to be resolved into a hydrate before it dissolves. Water decomposes it into sulphuric and hydrochloric acids: $S_2O_5Cl_2+3H_2O=2H_2SO_4+2HCl$; if the pyrosulphuryl chloride is contaminated with sulphur chloride, it deposits sulphur when decomposed by water, and emits a faint odour of sulphur dioxide. Analogous observations were made by H. E. Armstrong, and A. Michaelis; while D. Konowaloff said that the hydrolysis is energetic when the water is warm. W. Prandtl and P. Borinsky supposed the first stage of the reaction is: $S_2O_5Cl_2+H_2O=2HClSO_3$. G. Billitz and K. Heumann said that if 40 grms. of pyrosulphuryl chloride be warmed with 3 grms. of water between 154° and 158°, it is converted into pure chlorosulphonic acid, and added that this transformation slowly occurs in moist air since after a few days' exposure to moist air, the pyrosulphuryl chloride contains some chlorosulphonic acid. According to V. Grignard and P. Muret, sulphuryl chloride is hydrolyzed quickly by the action of a large excess of water, and conductivity measurements agree with the equation: $S_2O_5Cl_2+3H_2O=2H_2SO_4+2HCl$. The action is slow at first until the chloride has dissolved, but is increased by the presence of impurities produced during the preparation. With less water, two reactions occur, $S_2O_5Cl_2+H_2O=2HClO+2SO_2$, and $SO_2+2HClO=H_2SO_4+Cl_2$. In the presence of 1 to 3 mols of water per mol of chloride, the soln. has oxidizing properties. G. Carrara and I. Zoppelari said that the velocity of the reaction is such that if s is the surface area of the two liquids in contact; a, the quantity of pyrosulphuryl chloride; x, the quantity of the latter decomposed in the time t, $(1/st)\log\{a/(a-x)\}=ak$, where k is a constant equal to 0·00331 at 10°, and 0·0100 at 30°. H. Rose stated that pyrosulphuryl chloride absorbs **chlorine,** forming a yellowish-green liquid which smells strongly of chlorine, and evolves that gas with effervescence at 25°; it appears to boil at 112°, and becomes colourless again after the chlorine has escaped. A. Besson observed that pyrosulphuryl chloride reacts with dry **hydrogen bromide** at 50°, liberating sulphur dioxide and bromine, and forming chlorosulphonic acid, and the latter in turn is decomposed by the prolonged action of hydrogen bromide; **hydrogen iodide** in a vessel cooled by ice and salt furnishes similar products along with some hydrogen sulphide and sulphur. K. Heumann and P. Köchlin said that when pyrosulphuryl chloride is heated with flowers of **sulphur,** and distilled, it forms sulphur monochloride. The reaction was also studied by W. Prandtl and P. Borinsky. A. Besson found that it reacts slowly in the cold with **hydrogen sulphide,** and the main reaction is symbolized: $S_2O_5Cl_2+H_2S=S+2HCl+SO_3+SO_2$; and on heating, the reaction $3S_2O_5Cl_2+2H_2S=S_2Cl_2+HCl+3SO_2+3ClHSO_3$, which is secondary in the cold, becomes the chief or even the only reaction. H. Rose said that pyrosulphuryl chloride is miscible with **sulphur trioxide,** and the latter distils off first when the mixture is heated. W. Prandtl and P. Borinsky studied its action on **selenium** (*q.v.*), and **tellurium** (*q.v.*). F. Clausnizer observed that pyrosulphuryl chloride reacts with **selenium tetrachloride,** forming selenium pyrosulphochloride, $SeSO_3Cl_4$. H. Rose observed that when treated with dry **ammonia** it forms a white, dry mass which when treated with water furnishes equimolar parts of ammonium sulphate and chloride. K. Heumann and P. Köchlin observed that pyrosulphuryl chloride reacts with red **phosphorus,** forming phosphorus trichloride; A. Besson found that dry **phosphine** decomposes pyrosulphuryl chloride at ordinary temp., forming metaphosphoric acid, phosphorus tritetritasulphide, etc. H. E. Armstrong, A. Michaelis, and A. Geuther said that with **phosphorus pentachloride** it forms phosphoryl chloride, chlorine, and sulphur dioxide. Powdered **antimony** was found by K. Heumann and P. Köchlin to react vigorously with pyrosulphuryl chloride, forming sulphur dioxide and trioxide, antimony trichloride, and an antimony sulphate. A. Mente said that imidosulphurylamide is the first product of the action of **ammonium carbamate** on pyrosulphuryl chloride. K. Heumann and P. Köchlin found that with aromatic sulpho-acids an excess of pyrosulphuryl chloride furnishes disulphochlorides. A. Rosenstiehl found with **sodium acetate,** acetyl chloride, etc., are formed.

K. Heumann and P. Köchlin observed that pyrosulphuryl chloride reacts with

copper, zinc, or **iron,** forming the metal chloride and sulphur dioxide; A. Besson found that **mercury** is similarly attacked about 60°; and A. Ditte, that when heated with **gold,** auric chloride is formed. A. Rosenstiehl found that **manganates** react with pyrosulphuryl chloride, forming chlorine; while **chromates** form chromyl chloride. H. Rose heated a mixture of pyrosulphuryl chloride and **sodium chloride** and obtained a solid, transluscent mass which no longer fumes on exposure to air. When heated, some pyrosulphuryl chloride, mixed with chlorine, passes over, and the remainder is converted into chlorine, sulphur dioxide, and sodium pyrosulphate.

W. Traube found that a mol. of sodium chloride absorbs 2 mols. of sulphur trioxide, forming a hard crystalline mass of what is considered to be **sodium chloropyrosulphonate,** $NaO.SO_2.O.SO_2.Cl$, while sodium chlorosulphonate is probably an intermediate product of the reaction. It fumes in the air, and is decomposed by water, more slowly by alcohol. When added to a chloroform soln. of diamylamine, diamylamine sulphamate is formed, which agrees with the formulation of the salt as a chloropyrosulphonate. No evidence of the existence of the product $NaCl(SO_3)_4$ could be obtained. Ammonium chloride first liquefies under the action of sulphur trioxide, and then gives a crystalline product consisting of **ammonium chloropyrosulphate,** $NH_4O.SO_2.O.SO_2.Cl$. H. Rose, and A. W. Williamson said that ammonium chloride absorbs the vapour of sulphur trioxide without developing any gas, and produces ammonium chloropyrosulphate; when heated, it gives off hydrogen chloride. W. Traube obtained the salt having properties similar to that of the sodium salt. It cannot be the hydrochloride of a sulphamic acid, since the latter is not found in soln. when the salt is decomposed by alkali-lye. No evidence of the formation of A. Schultz-Sellack's $NaCl(SO_3)_4$ was observed.

J. Ogier [2] prepared what he regarded as **sulphur oxytetrachloride,** S_2OCl_4, by heating a mixture of sulphur monochloride and sulphuryl chloride in sealed tubes at 250° for several hours. On opening the tubes, sulphur dioxide is evolved in considerable quantity, and on distillation, the product yields a deep red liquid of lower boiling point than the two known oxychlorides, together with the excess of sulphur chloride, which contains dissolved sulphur. The red product is formed in accord with $2S_2Cl_2+2SO_2Cl_2=2S_2OCl_4+SO_2+S$. It is also obtained, although with greater difficulty, by heating sulphur monochloride at 250° with thionyl chloride saturated with chlorine, thus: $S_2Cl_2+Cl_2+2SOCl_2=2S_2OCl_4$. Sulphur oxytetrachloride is a deep red liquid, with an odour resembling that of sulphur chloride, but more penetrating. The sp. gr. is 1·656 at 0°, and the b.p. is 60°–61°. When heated, it decomposes even below 100° into sulphur monochloride, chlorine and sulphur dioxide. This dissociation prevents an accurate determination of the vapour density; but observations at as low a temp. as possible gave 3·87 (air unity). The oxytetrachloride is decomposed by water, with precipitation of sulphur, part of which is insoluble in carbon bisulphide, and formation of hydrochloric, sulphuric, and sulphurous acids, together with a notable quantity of thionic acid. The oxychloride reacts violently with absolute alcohol, hydrochloric acid, ethyl chloride, and sulphurous anhydride being evolved. The colourless liquid formed remains clear, but on distillation excess of alcohol first passes over, then a large quantity of sulphur is precipitated, and finally normal ethyl sulphite distils over at about 150°. Precipitation of sulphur is also caused by addition of a trace of water to the clear liquid. Possibly the alcoholic liquid contains the ester of an acid derived from S_2O_3. the oxychloride being formed from S_2O_3 by the substitution of Cl_4 for O_2. R. J. Knoll said that the alleged oxytetrachloride is really a mixture of sulphur dichloride, thionyl chloride, and sulphuryl chloride which cannot be easily separated into its constituents.

N. A. E. Millon [3] in his paper: *Sur l'acide hypochloreux et sur les chlorures de soufre,* described the preparation of what he called *chlorure de soufre cristallisé*—that is, according to the analyses of N. A. E. Millon, and of A. Michaelis and O. Schifferdecker, **sulphur trioxy-tetrachloride,** $S_2O_3Cl_4$, or $Cl.SO_2.O.SCl_3$, by the action of incompletely dried chlorine in great excess on sulphur or sulphur chloride: 20 to 30 grms. of sulphur chloride, saturated with chlorine, were introduced into a 4 to 5 litre-flask filled with moist chlorine; 2 to 3 grms. of water were added, and the mixture shaken. It was then allowed to stand 5 hrs. in a freezing mixture and moist chlorine passed in from time to time, and the operations repeated until a crystalline mass is formed. A stream of dry chlorine is passed over the warm mixture for 10-12 hrs. so as to remove the sulphur chloride; the crystals are heated, and sublimed into the upper part of the vessel. L. Carius prepared them by an analogous process, *viz.* by dropping sulphur monochloride into a flask filled with moist chlorine, when colourless crystals of this compound collect on the walls of the flask. A. Michaelis and O. Schifferdecker obtained the same compound by the action of sulphur tetrachloride on chlorosulphonic acid: A mol of sulphur monochloride and 2 mols of chlorosulphonic acid were introduced in a flask at −13° to −18°, and dry chlorine passed into the vessel until the mass had completely solidified; it was then removed from the freezing mixture and chlorine passed through the vessel until the crystalline mass became white. The compound was also prepared by W. Prandtl and P. Borinsky. Sulphur trioxytetrachloride forms fine needles, or transparent, colourless, rhomboidal plates. A. Michaelis and C. Mathias found that the vapour density is about one-half that indicated by the formula $S_2O_3Cl_4$, indicating a dissociation: $S_2O_3Cl_4=SOCl_2+SO_2Cl_2$. A. Michaelis and O. Schifferdecker found that the solid melts at 57° with decomposition giving off sulphur dioxide and chlorine leaving a residue of pyrosulphuryl and thionyl chlorides: $4S_2O_3Cl_4=S_2O_5Cl_2+5SOCl_2+2Cl_2+SO_2$. N. A. E. Millon said that when the crystals are fused they yield a mobile liquid which does not again solidify even at −18°, and the liquid and solid are supposed to be isomerides. A. Michaelis and co-workers also found that when the solid has been kept for some time—2 or 3 months—it changes into a yellow liquid which is identical in composition with the solid. Assuming that the solid has the constitution $Cl.SO_2.O.SCl_3$, the liquid may be the theoretical isomeride, $Cl.SO.O.SOCl_3$. The liquid distils at 73°. According to N. A. E. Millon, the crystals are vigorously decomposed by alcohol, dil. acids, or water, and by moist air; the liquid, also, when digested with water decomposes slowly, forming sulphurous, sulphuric, and hydrochloric acids: $Cl.SO_2.O.SCl_3+4H_2O=H_2SO_4+H_2SO_3+4HCl$. A. Michaelis and O. Schifferdecker also noted the formation of sulphur by the action of cold water on the solid, and L. Carius added that thiosulphuric acid is also produced. A. Michaelis and O. Schifferdecker said that the crystals dissolve in warm sulphur monochloride. When the liquid is distilled with sulphur trioxide, A. Michaelis and C. Mathias said that pyrosulphuryl and sulphuryl chlorides are formed. As thionyl chloride is decomposed by sulphur trioxide, with the production of pyrosulphuryl chloride, while sulphuryl chloride is unacted upon under the same circumstances, it is concluded that the liquid consists of a mixture of equimolar proportions of thionyl chloride and sulphuryl chloride, $S_2O_3Cl_4=SOCl_2+SO_2Cl_2$. Sulphur trioxytetrachloride is therefore in all probability a molecular combination, which may exist either as a solid or a liquid. The reaction with carbon disulphide is symbolized: $5CS_2+7S_2O_3Cl_4=3COCl_2+2CO+6SO_2+7S_2Cl_2+4SOCl_2$.

P. Schützenberger[4] passed chlorine monoxide over 5 to 6 grms. of sulphur trioxide when the solid becomes warm, and melts to a dark red liquid which, on cooling, forms red needles resembling chromic acid. The composition is **tetra-anhydrosulphatochlorine monoxide,** $Cl_2O.4SO_3$. The crystals melt at 55°; they detonate when heated; decompose into hypochlorous and sulphuric acids when treated with water; oxidize organic substances; and react with iodine, forming iodic acid and chlorine. This product has not been interpreted further.

According to A. Bussy,[5] sulphur trioxide reacts with iodine, forming a greenish-blue liquid; N. W. Fischer said that the product is sometimes brown, sometimes green, and sometimes blue; the green and blue colours are transient, the brown, persistent. G. F. Wach said that with the minimum quantity of trioxide the colour is brown, with a larger quantity blue, and with a still larger quantity green. He said:

> If a bent glass tube with one part of iodine in one leg, and two parts of trioxide in the other, be sealed, and heat applied to the arm containing the trioxide, the first portion of vapour forms with the iodine a viscid brown liquid, and by taking up more trioxide it becomes a green, crystalline solid. The crystals melt at 37° to an oily liquid, and solidify at 12·5° to a fibrous mass; the product boils at 107·5°, and sulphur trioxide distils into the other arm, where it forms a white, crystalline mass; and the liquid as it parts with the acid becomes blue and afterwards brown. The iodine finally sublimes, forming a green

product with the sulphur trioxide. If one arm of the tube contains 1 part of iodine and 1 part of sulphur, the other, 20 parts of sulphur trioxide, and the whole is left to stand overnight at the ordinary temp. of the air, the sulphur acquires a carmine colour. If the sulphur trioxide arm be warmed, while the other arm is kept in a freezing mixture, the sulphur and iodine form a thin red-brown liquid, which moves about as if it were boiling, and gradually becomes, first brown, then brownish-green, and crystallizes. When taken out of the freezing mixture, it changes in the course of four weeks to a beautiful green liquid, which crystallizes in the cold. Sulphur dioxide may be distilled from it, but when separated in this manner, may be made to recombine with the residue.

According to R. Weber, dry powdered iodine is absorbed by sulphur trioxide, heat is developed, and a dark greenish-brown viscid liquid is formed, and settles below the colourless sulphur trioxide remaining in excess. By pouring off the latter at a suitable temp., there remains **iodine trianhydrosulphate,** $I(SO_3)_3$, as a crystalline mass which fumes in air. If this compound be heated on a water-bath it loses some sulphur trioxide, forming **iodine anhydrosulphate,** ISO_3, as a viscid mass which fumes in air, and which decomposes, with the separation of iodine, when treated with water. If either $I(SO_3)$, or $I(SO_3)_3$, be heated near 170°, there remains **iodine hemianhydrosulphate,** $I_2(SO_3)$, which is solid at ordinary temp., and decomposed by water. A. C. Schultz-Sellack also obtained crystals of this substance by the action of the vapour of sulphur trioxide on iodine. If the sulphur trioxide used in these preparations contains a little hydrate, the product is blue, and with more hydrate it becomes green and then brown.

H. Kämmerer, and C. Winkler said that dry sulphur dioxide acts at 100° on powdered iodine pentoxide, forming what appears to have been a product with the composition *iodine pentitanhydrosulphatopentoxide*, $5I_2O_5.SO_3$. A. Ditte denied the existence of this as a chemical individual. R. Weber, and R. Knietsch heated a mixture of dried iodine pentoxide and sulphur trioxide on a water-bath, and obtained yellow plates of *iodine trianhydrosulphatopentoxide*, $I_2O_5.3SO_3$, which are stable up to 60°, but give off sulphur trioxide at a higher temp.

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§ 53. Halogenosulphonic Acids and their Salts

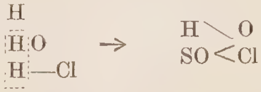
According to G. Gore,[1] liquid hydrogen fluoride unites with sulphur trioxide with a hissing noise, with the development of heat, and with the formation of a colourless. mobile liquid approximating in composition $SO_3.6HF$, and probably a soln. of **fluosulphonic acid,** $HFSO_3$, or $HO.SO_2.F$, in hydrogen fluoride. L. Pfaundler also observed that gaseous hydrogen fluoride is absorbed by sulphuric acid, and is expelled when the soln. is heated; G. Gore found that at —18° to —29°, liquid hydrogen fluoride mixes quietly with conc. sulphuric acid. T. E. Thorpe and W. Kirman distilled sulphur trioxide into a weighed platinum receiver; an excess of hydrogen fluoride was distilled into the same vessel cooled by a mixture of ice and calcium chloride. The uncombined hydrogen fluoride was removed by passing a current of carbon dioxide through the vessel heated to a temp. of 25°–35°. The analysis of the remaining liquid agreed with that required for fluosulphonic acid. O. Ruff and H. J. Braun observed that when fluorspar is heated with 97–100 per cent. sulphuric acid, a 60 per cent. yield of hydrofluoric acid is obtained; with sulphuric acid containing a high percentage of sulphur trioxide—50–60 per cent. —the product no longer contains hydrofluoric acid, but consists only of fluosulphonic acid: $CaF_2+H_2SO_4+2SO_3=CaSO_4+2F(HSO_3)$; and with sulphuric acid containing 60 per cent. of sulphur trioxide, a quantitative yield of fluosulphonic acid is obtained. The reaction was studied by W. Traube and W. Lange. W. Traube obtained fluosulphonic acid by distillation from a mixture of fuming sulphuric acid and ammonium fluoride; or from a fluosulphonate and 99 per cent. sulphuric acid.

T. E. Thorpe and W. Kirman said that fluosulphonic acid is a thin, colourless liquid which fumes in air; it has a faint, pungent smell, and has but little action on the dry skin; it feels greasy to the touch, and is without the intense blistering action of hydrofluoric acid. Fluosulphonic acid boils at 162·6°, and, like chlorosulphonic acid, it cannot be distilled without more or less decomposition, forming presumably some sulphuryl fluoride, $2F(HSO_3)=SO_2F_2+H_2SO_4$. O. Ruff could not confirm this hypothesis since he found that the acid is stable even at 900°. The b.p. of fluosulphonic acid is higher than that of chlorosulphonic acid, as that of hydrogen fluoride is higher than that of hydrogen chloride. Fluosulphonic acid is decomposed by water with almost explosive violence. W. Traube and E. Reubke showed that the reaction, in not too dil. aq. soln., is a balanced one, $F(HSO_3)+H_2O\rightleftharpoons H_2SO_4+HF$. The formation of fluosulphonic acid from mixtures of 62 per cent. hydrofluoric acid, and 94 per cent. sulphuric acid is readily demonstrated by mixing the two acids cooled to —20°. O. Ruff represented the reaction which occurs when fluosulphonic acid is boiled with sulphur by: $2F(HSO_3)+S=3SO_2+2HF$. W. Traube and E. Brehmer prepared a series of amidosulphonic acids by the action of fluosulphonate on aq. ammonia and the substituted ammonias; likewise hydrazinosulphonates were made by the action of fluosulphonate on hydrazine. Fluosulphonic acid was found by T. E. Thorpe and W. Kirman to attack glass slowly, but more rapidly in the presence of moist air. O. Ruff observed that fluosulphonic acid acts on potassium permanganate, yielding a violet vapour which decomposes on contact with air. T. E. Thorpe and W. Kirman observed that fluosulphonic acid quickly acts on lead, forming lead sulphate and fluoride.

Fluosulphonic acid, $HO.SO_2.F$, acts as a monobasic acid, forming a series of stable salts, **fluosulphonates.** W. Lange found that the crystals of fluosulphonates are analogous chemically, and in part crystallographically with the perchlorates and permanganates. W. Traube and co-workers prepared crystals of **ammonium**

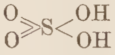
fluosulphonate, $NH_4O.SO_2.F$, or $NH_4SO_3.F$, by the action of sulphur trioxide on ammonium fluoride; treating the product with ammoniacal methyl alcohol; and evaporating the soln. If dry ammonium fluoride is gradually dissolved in fuming sulphuric acid containing 70 per cent. SO_3; the soln. treated with ammoniacal methyl alcohol, and separated from the insoluble matters—mainly ammonium sulphate—a soln. of ammonium fluosulphonate is formed, and this yields the crystalline solid on evaporation. Ammonium and alkali fluosulphonates are formed when a dry mixture of fluorides and pyrosulphates is heated, and when the two are mixed in the presence of a little water. The best yields are obtained from potassium pyrosulphate and an excess of ammonium fluoride; the yield is appreciably less when the latter is replaced with potassium fluoride, and still less with sodium fluoride. Fluosulphonates are also obtained by compressing a mixture of the fluoride and pyrosulphate particularly in the presence of a little water; and by heating mixtures of ammonium persulphate and fluoride. The m.p. of ammonium fluosulphonate is 245°. Its aq. soln. reacts neutral to litmus, and it is not decomposed after keeping for many days; and the salt can even be recrystallized from hot water. The fluosulphonates are readily decomposed by warming with hydrochloric acid, forming hydrofluoric and sulphuric acids; but they are more stable in alkaline soln. When distilled with 99 per cent. sulphuric acid, they yield fluosulphonic acid. Ammonium fluoride readily reacts with gaseous ammonia, particularly at low temp., forming liquid ammines; and with aq. ammonia, or substituted ammonias, the fluosulphonates yield aminosulphonates; and with hydrazine, hydrazinosulphonates. W. Lange prepared salts with tetramethylammonium, *o*-toluenediazonium, benzenediazonium, pyridinium, nitron, strychnine, brucine, morphine, and cocaine. W. Traube and co-workers found that the alkali fluosulphonates are obtained by the action of the requisite alkali hydroxide on an aq. soln. of the ammonium salt. Long shining needles of **lithium fluosulphonate,** $LiSO_3F.3H_2O$, melting at 60°–61°, were so obtained; the anhydrous salt melts at 360°. A mol. of sodium fluoride absorbs a mol. of sulphur trioxide, forming **sodium fluosulphonate,** $NaSO_3F$, which can be readily dissolved from unaltered sodium fluoride by extraction with alcohol. The salt is also obtained by the method indicated for the ammonium salt, and by the direct action of an alkali hydroxide on an aq. soln. of fluosulphonic acid, proving that the acid is not immediately decomposed by water. O. Ruff made sodium fluosulphonate by heating 50 grms. of fluosulphonic acid and 92·2 grms. of sodium chloride in a platinum retort under a reflux condenser for half an hour, and extracting the product with boiling absolute alcohol. The resulting soln. yields iridescent plates or needles of sodium fluosulphonate on cooling. W. Traube and co-workers found that the aq. soln. of sodium fluosulphonate, like that of the ammonium salt, is neutral to litmus; and it reacts similarly with acids and alkalies. When heated in an atm. of carbon dioxide, it furnishes a gas thought to be sulphuryl fluoride: $2NaSO_3F=Na_2SO_4+SO_2F_2$. Short, stout prisms of **potassium fluosulphonate,** KSO_3F, were obtained melting at 311°; crystals of **rubidium fluosulphonate,** $RbSO_3F$, melting at 304°; W. Lange prepared rhombic, pseudotetragonal crystals of **cæsium fluosulphonate,** $Cs(FSO_3)$, melting at about 292°; water at 0° dissolves 2·23 grms. per 100 c.c. of soln.; anhydrous and dehydrated **copper tetramminofluosulphonate,** $Cu(SO_3F)_2.4NH_3.2H_2O$, melting at 55·6°; water at 12° dissolves 52·9 grms. per 100 c.c. W. Lange also prepared the bisethylenediamine salt, $Cu(SO_3F)_2.2en,\frac{1}{2}H_2O$, and the pyridine salt, $Cu(SO_3F)_2.4C_5H_5N$. W. Traube and co-workers prepared impure **barium fluosulphonate,** $Ba(SO_3F)_2$; all the fluosulphonates, except the nitron salt, are freely soluble in water. The alkali fluosulphonates are very stable towards heat. Thus, the potassium salt only suffered a slight decomposition with the evolution of sulphur dioxide and trioxide, hydrogen fluoride, and oxygen when heated to bright redness. Crude barium fluosulphonate, on the other hand, is decomposed at a red-heat into sulphuryl fluoride and barium sulphate. W. Lange found that the fluosulphonates of the heavy metals are freely soluble in water, and are too easily hydrolyzed to permit their isolation. The fluosulphonates become stable and crystalline when the size of the cation is increased by complex formation with ammonia or the amines.

In 1856, A. W. Williamson [2] defined, if not discovered, **chlorosulphonic acid,** HSO_3Cl, or $HO.SO_2.Cl$, and it attracted some attention about that period because, on the old theory of types—**1.** 5, 16—it was the first example of a mixed type—the water type and the hydrochloric acid type united by the bivalent SO_2-radicle :



$$\begin{matrix} H & \\ H & O \\ H & —Cl \end{matrix} \rightarrow \begin{matrix} H\diagdown O \\ SO<Cl \end{matrix}$$

The name chlorohydrines was applied to combinations of this mixed type, so that chlorosulphonic acid is also called *sulphuric chlorohydrine,* and it has also been called *chlorosulphuric acid, chlorohydrated sulphuric acid,* and *chlorohydrosulphurous acid.* Analyses by A. W. Williamson, F. Baumstark, F. Clausnizer, J. Ogier, and S. Williams agree with the formula $ClHSO_3$. K. Heumann and P. Köchlin, J. Ogier, S. Williams, and F. Baumstark found the vapour density to be in agreement with the formula $ClHSO_3$. M. Müller said that chlorosulphonic acid unites with ethylene with the evolution of much heat, forming ethyl chlorosulphonate, $C_2H_5SO_3.Cl$, a colourless mobile liquid boiling at 93°–95° under 100 mm. press. It is decomposed by hot water into hydrochloric and sulphuric acids, and alcohol. Hence, its formula is more likely to be $Cl.S.O.O.OC_2H_5$ than $C_2H_5O.S.O.O.Cl$, because the latter would probably form ethyl sulphate and hydrochloric acid when hydrolyzed by water. This led M. Müller to favour the formula Cl.S.O.O.OH. Sulphur trioxide was also found to react with ethyl chloride, forming amongst other substances ethyl chlorosulphonate. T. von Purgold also studied the products of this reaction. These results show that the chlorine is probably united directly with the sulphur. F. W. Bushong found that the ethyl chlorosulphonate prepared by J. U. Nef by the action of phosphorous pentachloride on ethylsulphuric acid is identical with that prepared by P. Behrend by the action of sulphuryl chloride on ethyl alcohol. The various reactions of chlorosulphonic acid—*e.g.* the formation of hydrochloric and sulphuric acids—show that it is closely related to sulphuric acid, so that the two have analogous formulæ. If the sulphur atom in sulphuric acid be sexivalent—*vide supra*—the formula of the acid will be $HO.SO_2.Cl$, or



$$\begin{matrix} O \\ O \end{matrix}\!\!>\!S\!<\!\!\begin{matrix} OH \\ OH \end{matrix}$$

A. W. Williamson prepared chlorosulphonic acid by the direct action of hydrogen chloride on sulphur trioxide : $SO_3+HCl=ClHSO_3$. The General Electric Co. used a similar process ; H. Beckurts and R. Otto, P. Claesson, A. Michaelis and O. Schifferdecker, M. Müller, T. I. Briggs, and P. Behrend, utilized the action of hydrogen chloride on fuming sulphuric acid—say by passing a vigorous stream of hydrogen chloride into 200 grms. of 80 per cent. fuming sulphuric acid contained in a large flask with ground glass-joints at ordinary temp. ; when the flask becomes warm, it should be cooled with ice. When hydrogen chloride is no longer absorbed, the product is distilled in a flask fitted with an air condenser. Some dissolved hydrogen chloride first escapes, and the distillate collected between 150° and 165° is redistilled and the fraction collected at 153°. M. Müller made the acid by distilling fuming sulphuric acid with phosphorus pentoxide in a current of hydrogen chloride : $H_2SO_4+P_2O_5+HCl=2HPO_3+ClHSO_3$; A. W. Williamson, S. Williams, J. Dewar and G. Cranston, F. Baumstark, and A. Michaelis, by the action of phosphorus tri- or penta-chloride, or phosphoryl chloride on conc. sulphuric acid, thus, $2H_2SO_4+PCl_3=HPO_3+2HCl+SO_2+ClHSO_3$, $H_2SO_4+PCl_5=ClHSO_3+POCl_3+HCl$, and $POCl_3+2H_2SO_4=HPO_3+HCl+2Cl(HSO_3)$. The preparation is as follows : 150 grms. of phosphorus pentachloride are gradually introduced into 200 grms. of fuming sulphuric acid of sp. gr. 1·84 at 15°. The mixture becomes warm, and much hydrogen chloride escapes. The flask is then heated until no more of this gas is evolved. The liquid is then distilled, and purified by redistillation as before. T. E. Thorpe heated a mixture of 226 grms. of phosphoryl chloride and 200 grms. of the most conc. sulphuric acid, and collected the fraction distilling between 153° and 154°. This was rectified by redistillation. A. W. Williamson obtained chlorosulphonic acid by the action of chlorine or sulphur chloride on conc. sulphuric acid; C. Moureu, by the action of sulphuric acid on thionyl chloride; W. Odling, by the action of moisture on sulphuryl chloride: $SO_2Cl_2+H_2O=HCl+HO.SO_2.Cl$; A. Michaelis, by the action of a little water or conc. sulphuric acid on sulphuryl chloride; by G. Billitz and K. Heumann, and J. Ogier, by the action of water on pyrosulphuryl chloride; and R. Railton, and W. Odling by the action of imperfectly dried chlorine on moist sulphur dioxide in the presence of platinum-black, and at a red-heat.

Chlorosulphonic acid is a colourless, fuming liquid with a piquant odour, and it exerts a corrosive action on the skin. F. Baumstark said that the liquid is slightly yellow. W. Michaelis said that the **specific gravity** is 1·776 at 18°; P. Walden, 1·7875 at 25°; and T. E. Thorpe, 1·78474 at 0°, and 1·54874 at the b.p. 155·3°. The **molecular volume** is therefore 75·05 at the b.p. F. Baumstark gave 4·08–4·12 for the **vapour density** when the calculated value is 4·04; at 216°, S. Williams obtained a vap. density of 2·27 indicating some dissociation: $2ClHSO_3=SO_3+SO_2+H_2O+Cl_2$. K. Heumann and P. Köchlin found 2·39 to 2·42 at 184·4°; and 2·09 at 444°; while J. Ogier gave 2·36 to 2·46 between 180° and 216°. The **thermal expansion** of the liquid was represented by T. E. Thorpe in terms of the vol. v at θ° occupied by unit vol. at 0°, when $v=1+0{\cdot}000905\theta+0{\cdot}0_6118647\theta^2+0{\cdot}0_823943\theta^3$. J. Ogier gave 0·282 for the **specific heat** between 15° and 80°. A. W. Williamson found the **boiling point** to be 145°; A. Michaelis, 158·4°; P. Behrend, 153°; H. Beckurts and R. Otto, 150·7° to 152·7°; T. E. Thorpe, 155·3°; W. Clausnizer, between 150° and 151° at a press. of 726 mm. and the b.p. is reduced one degree when the press. is reduced by 20·6 mm. P. Walden gave 78° at 21–22 mm. press. According to A. W. Williamson, the liquid is partially decomposed into hydrogen chloride and sulphur trioxide at the b.p., and W. Odling said into sulphuric acid and sulphur chloride. F. Clausnizer found that when heated for a long time in a reflux condenser, it is partly decomposed into sulphuric acid, sulphur dioxide, and chlorine. F. W. Lauer discussed this subject. J. Ogier gave 12·8 Cals. for the **heat of vaporization**; and for the **heat of formation**: $SO_{3solid}+HCl_{gas}=ClHSO_{3liquid}+14{\cdot}4$ Cals.; and $SO_{3gas}+HCl_{gas}=ClHSO_{3gas}+13{\cdot}4$ Cals.; and $S_2O_5Cl_2+H_2O=2ClHSO_3+54$ cals. P. Walden found that the sp. **electrical conductivity** of the acid at 25° is $0{\cdot}0_3172$ and in vacuo $0{\cdot}0_3162$, and he found that it is an ionizing solvent. The conductivity of a soln. of potassium bromide decreases from 23·51 with $v=146$ to 20·68 with $v=490$. Chlorosulphonic acid dissolves many inorganic salts relatively easily; tetraethyl-ammonium iodide forms a deep brown soln., tetraethyl-ammonium bromide, potassium bromide, and anhydrous cobalt bromide form pale yellow soln. which gradually darken.

According to A. W. Williamson, and A. Michaelis, when poured into **water**, it sinks to the bottom and gradually dissolves with the formation of sulphuric and hydrochloric acids; each drop of acid, falling into cold water, reacts violently as in the case of sulphur trioxide. A. W. Williamson found that chlorosulphonic acid dissolves **sodium chloride** at a gentle heat evolving hydrogen chloride and forming sodium chlorosulphonate; for the action on **potassium bromide**, *vide supra*. K. Heumann and P. Köchlin found that chlorosulphonic acid does not react with **sulphur** at ordinary temp., but when warmed there is a vigorous reaction and sulphur dioxide, sulphur monochloride, and sulphuric and hydrochloric acids are formed. H. Prinz observed that **hydrogen sulphide** acts on the cold acid with the separation of sulphur and the formation of hydrogen chloride, and on distilling the liquor, sulphur monochloride and sulphuric acid are formed. S. Williams found that with conc. **sulphuric acid,** hydrogen chloride and fuming sulphuric acid are formed. H. Schiff represented the reaction with molten **potassium sulphate :** $K_2SO_4+ClHSO_3=K_2S_2O_7+HCl$. F. Clausnizer observed that selenium sulphotrioxytetrachloride, $SO_3.SeCl_4$, is formed when chlorosulphonic acid reacts with **selenium dioxide, tetrachloride,** or **oxydichloride.** According to A. Mente, **ammonium carbamate** forms $NH(SO_2.ONH_4)_2$, when treated with chlorosulphonic acid. A. W. Williamson said that chlorosulphonic acid reacts with **sodium nitrate** to form nitroxyl chloride : $NaNO_3+ClHSO_3=NaHSO_4+NO_2Cl$. W. C. Williams observed that when dry fused potassium nitrate is treated with chlorosulphonic acid, the mixture becomes hot, and chlorine escapes ; he represented the reaction $2ClHSO_3+2KNO_3=N_2O_4+Cl_2+2KHSO_4$, and $ClHSO_3+N_2O_4=HNO_3+Cl.SO_2.O.NO$; and when heated with an excess of potassium nitrate, $2(Cl.SO_2.O.NO)+2KNO_3=3N_2O_4+Cl_2+2K_2SO_4$. T. E. Thorpe found that with **silver nitrate** there is a vigorous reaction, and silver chloride and nitroxyl chlorosulphonate, $NO.O.SO_2.Cl$, are formed. K. Heumann and P. Köchlin observed that **phosphorus** is converted into chloride by the acid ; A. Michaelis represented the reaction of a mol of **phosphorus pentachloride** and 2 mols of chlorosulphonic acid by $PCl_5+2ClHSO_3=S_2O_5Cl_2+2HCl+POCl_3$; and with equimolar parts, sulphur dioxide, hydrogen chloride, and phosphoryl chloride are formed. G. Billitz and K. Heumann, and D. Konowaloff observed that when the acid is heated with **phosphorus pentoxide,** pyrosulphuryl chloride, $(Cl.SO_2)O_2$, is formed as an anhydride of chlorosulphonic acid. Chlorosulphonic acid converts **arsenic** and **antimony** into their chlorides. F. Clausnizer found that equimolar parts of chlorosulphonic acid and **antimony pentachloride,** (*q.v.*) form a greenish liquid ; and the acid dissolves a little **antimony trichloride** (*q.v.*) at ordinary temp.

K. Heumann and P. Köchlin found that when heated with **carbon** at a high temp., sulphur dioxide, carbon mono- and di-oxides, and hydrogen chloride are formed. According to J. Dewar and G. Cranston, chlorosulphonic acid does not mix with **carbon disulphide ;** in a sealed tube at 100°, they unite with the separation of sulphur, and the reaction is symbolized : $CS_2+ClHSO_3=HCl+SO_2+COS+S$. G. Billitz and K. Heumann, and D. Konowaloff also investigated the reaction. M. Müller found that **ethylene** unites with chlorosulphonic acid, forming ethyl chlorosulphonate. K. Knapp, and R. Pummerer observed that with **benzene,** the sulphochloride, and sulphonate are formed. H. E. Armstrong, and K. Heumann and P. Köchlin observed that chlorosulphonic acid acts as a chlorinating agent transforming **sulphonates** into sulphochlorides—*e.g.* magnesium *o*-toluosulphonate into *o*-toluol sulphochloride ; **sodium acetate** into acetyl chloride ; and **sodium benzoate** into benzoyl chloride. F. Baumstark studied the action on **acetic acid** which results in the formation of hydrogen chloride, methylenedisulphonate, and glycolsulphonate. P. Claësson observed that monohydric and polyhydric **alcohols** form ethereal sulphates. D. McIntosh found that at low temp. —50° to —80°, ethyl hydrosulphate and hydrogen chloride are formed while **ether** yields the addition product $(2(C_2H_5)_2O.HSO_3Cl$, and **acetone,** $2C_2H_5.COH.HSO_3Cl$. J. Dewar and G. Cranston found that in a sealed tube at 120°, **chloroform** reacts : $CHCl_3+Cl(HSO_3)=COCl_2+SO_2+2HCl$. C. Boulin and L. J. Simon studied the action of chlorosulphonic acid on **dimethyl sulphate ;** and K. G. Naik and M. B. Amin, its action on **cyanacetic acid.**

F. Clausnizer observed that chlorosulphonic acid does not react with **silicon tetrachloride** in sunlight or at 170° ; but it reacts with **titanium tetrachloride,** forming the complex $TiCl_4.SO_3$, or $Cl.SO_2.O.TiCl_3$. K. Heumann and P. Köchlin found that **tin** is directly chlorinated by chlorosulphonic acid. F. Clausnizer found that chlorosulphonic acid mixes but does not react with **stannic chloride.**

Chlorosulphonic acid has the general properties of a monobasic acid, forming definite salts—**chlorosulphonates**—in which the hydrogen of the acid is replaced by a metal. W. Odling obtained **sodium chlorosulphonate,** $ClNaSO_3$, as indicated above. M. Müller said that the chlorosulphonates are difficult to prepare ; they are decomposed by water into hydrosulphate and hydrochloric acid ; and by alcohol into ethyl sulphate and hydrochloric acid. When heated, they decompose into chlorine, sulphur dioxide, and sulphate.

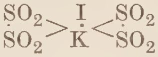
Attempts to make **bromosulphonic acid,** $BrHSO_3$, or $BrSO_2.OH$, have not been successful. G. Aimé[3] found that sulphur trioxide absorbs hydrogen bromide, forming a red liquid; and, according to F. Clausnizer, there is a reaction: $SO_3+2HBr=SO_2+H_2O+Br_2$, when a soln. of phosphorus pentabromide in sulphuric acid is distilled, bromine volatilizes and a mixture of sulphuric and phosphoric acids remains.

It is doubtful if **iodosulphonic acid,** $IHSO_3$, or $I.SO_2.OH$, has been prepared. S. Zinno[4] found that sulphur dioxide decolorizes starch iodide, and furnishes an acid like that obtained by T. J. Pelouze and E. Frémy by distilling a dried mixture of iodine and lead sulphite, and rectifying the distillate over mercury. S. Zinno tried to prepare iodosulphonates by the action of a sulphite on starch iodide, but could not obtain the product free from starch. Iodine can be dissolved with a slight evolution of heat in sodium or potassium sulphite, and by cooling the soln. after each addition of iodine as long as it is decolorized; evaporating the soln. at a gentle heat, he obtained a salt identical with that produced by the action of a sulphite on starch iodide. Iodosulphonic acid was made by the action of iodine on a conc. aq. soln. of sulphurous acid, and neutralized with an alkali carbonate. The liquid furnished alkali iodosulphonates. The iodosulphonates were also prepared by dissolving iodine in soln. of alkali thiosulphates, but the best results were obtained by adding iodine in small portions at a time to a cold soln. of an alkali sulphite, avoiding a rise of temp., and evaporating the liquid at a moderate heat in a dark place protected as much as possible from the action of air. In this manner S. Zinno prepared what he regarded as **ammonium iodosulphonate, potassium iodosulphonate,** and **sodium iodosulphonate.** The latter salt was partly analyzed. The salts are said to be isomorphous, soluble in water, and rapidly decomposed by air and by light.

It is said that sodium iodosulphonate, $Na_2I_2SO_3.10H_2O$, or possibly $INaSO_3.10H_2O$, crystallizes in colourless, long, symmetrical prisms; it has a bitter taste, which is, however, less disagreeable than that of the sulphate; it is readily soluble in water: 100 parts of water dissolve 27·5 parts of the salt at 15°; it is also very soluble in alcohol. When heated, it gives off iodine, and is converted into sodium sulphide and sulphate. A soln. of the salt in water does not react alkaline, and is decomposed by a weak electric current into hydriodic acid, sulphuric acid, and soda. Sulphuric acid decomposes it with evolution of sulphur dioxide and iodine vapour. Nitric acid precipitates iodine; mercuric nitrate produces a yellowish-white, silver nitrate a dirty-white, and lead acetate a white precipitate. Hydrochloric acid liberates the free acid with formation of sodium chloride. A soln. of mercuric chloride produces a white precipitate, which changes to pink and red, and is soluble in excess of the reagent. Baryta-water gives a white precipitate, which dissolves almost entirely in hydrochloric acid. Cupric sulphate produces, after a time, a greenish-white, auric chloride, a very dark brownish-red precipitate; metallic gold and silver even are acted upon by a soln. of sodium iodosulphonate.

A. Michaelis and G. Köthe denied the existence of S. Zinno's iodosulphonates. They said that sodium sulphite and lead iodide form sodium iodide and lead sulphite; and that sulphurous acid decomposes lead iodide, forming lead sulphite and hydriodic acid. According to R. Weber, fuming sulphuric acid readily dissolves iodine, forming a brown soln.—*vide supra*—but only a little iodine dissolves in ordinary sulphuric acid; and G. Aimé said that sulphur trioxide readily dissolves hydrogen iodide, forming a reddish-brown liquid. For P. Chrétien's iodine sulphate $I_2O_3.SO_3.\frac{1}{2}H_2O$—*vide* **2.** 19, 7; N. A. E. Millon's sulphate—see **2.** 19, 9; N. A. E. Millon also reported a complex **iodatosulphuric acid,** $2HIO_3.3H_2SO_4$, from a soln. of iodic acid and boiling, conc. sulphuric acid (5 : 1), and the *trihydrate*, $2HIO_3.3H_2SO_4.6H_2O$, from a soln. of iodic acid in sulphuric acid—$H_2SO_4.2H_2O$.

The tendency of sulphur dioxide to form complexes has been previously discussed. C. J. J. Fox[5] obtained evidence of the formation of *cadmium sulphuryl iodide*, as well as of *ammonium, sodium, potassium, and cadmium sulphuryl bromides, sulphuryl chlorides, sulphuryl nitrates, and sulphuryl thiocyanates*, but not of *sulphuryl* *sulphate.* E. Péchard prepared **sulphuryl hydroiodide,** $SO_2.HI$—possibly *iodosulphinic acid,* $I(HSO_2)$—for he found that when sulphur dioxide is passed into an aq. soln. of potassium iodide, the liquid becomes yellow, and finally orange. If the gas be passed over the solid salt, at 0°, potassium sulphuryliodide, or potassium iodosulphinate, $I(KSO_3)$, is formed. When this salt is heated to 100°, it loses the absorbed sulphur dioxide. The vap. press. of the compound is 600 mm. at 0°; 930 mm. at 10°; 1460 mm. at 20°; and 2380 mm. at 30°. Sodium, ammonium, silver, calcium, and barium iodosulphinates were similarly obtained. E. Ephraim and I. Kornblum also made complexes with alkali and calcium thiocyanates. R. de Forcrand and F. Taboury obtained **sodium, rubidium,** and **cæsium trisulphuryliodides** of the type $MI.3SO_2$, from liquid sulphur dioxide and the corresponding iodides, but F. Ephraim doubted if these products are chemical individuals. F. Ephraim and I. Kornblum obtained two series of complex iodides—yellow and red—and they were supposed to represent the existence of isomerides, $[M(SO_2)_4][(SO_2)_4MI_2]$, and $[M(SO_2)_6][(SO_2)_2MI_2]$. The dichromate-coloured lithium sulphuryl iodide $I(LiSO_2)$, is formed at 0°; and **lithium disulphuryliodide,** $LiI.2SO_2$, at a lower temp. Red **sodium disulphuryliodide,** $LiI.2SO_2$, is formed at 0°; and **sodium tetrasulphuryliodide,** $NaI.4SO_2$, is formed in a freezing mixture. P. Walden and M. Centnerszwer found that when dry trimethylsulphonium iodide or potassium thiocyanate is exposed to the action of sulphur dioxide gas, there is an increase in weight and a change in the appearance of the salt. With potassium, sodium, ammonium, and tetramethylsulphonium iodides and with ammonium and sodium thiocyanates no change was observed. It is assumed that any compounds which might be formed are too unstable at ordinary temp. A 20 per cent. soln. of potassium iodide in sulphur dioxide is liquid at ordinary temp. but it gives red crystals when cooled in a mixture of snow and salt. The analysis corresponded with **potassium tetrasulphuryliodide,** $KI.4SO_2$.



$$\begin{matrix}SO_2\\SO_2\end{matrix}>\underset{K}{\overset{I}{\vdots}}<\begin{matrix}SO_2\\SO_2\end{matrix}$$

The f.p. curve of mixtures of potassium iodide and sulphur dioxide is shown in Fig. 151. *A*, —72·7°, is the f.p. of sulphur dioxide; *B*, the eutectic with 0·34 mol per cent. of potassium iodide; between *BC*, a yellow crystalline powder of **potassium tetradecasulphuryl iodide,** $KI.14SO_2$, separates on cooling, and *C* is a maximum at —23·4° with about 8 molar per cent. of KI; there is a second eutectic *D*; and red crystals of the tetrasulphuryl iodide separate on cooling along the branch *DE*. The f.p. of this compound, 0·26°, is represented by *E*. The soln. separates into two layers on heating, and, on further heating, well-formed, yellow crystals are deposited, and one of the liquid phases disappears; on cooling, the corresponding reverse changes are observed. From the phase rule, it follows that the temp. at which the solid phase is in equilibrium with the two liquid phases must be independent of the conc.; this temp. is 88·1°. Dil. and conc. soln. of potassium iodide deposit solid on heating without the intermediate formation of two liquid phases. *EG* represents mixtures of potassium iodide with molten potassium tetrasulphuryliodide, and on the left of *EG*, homogeneous soln. of potassium iodide in sulphur dioxide; *GH*, the equilibrium line for soln. and solid potassium iodide; *H* represents the upper limiting temp. of soln. of potassium iodide; below this, the soln. separates into two layers. Beyond *H*, and on *JK*, potassium iodide separates out. The stippled portion of Fig. 150 represents the region of homogeneous soln. The existence of the tetrasulphuryliodide was confirmed by measurements of the vap. press.

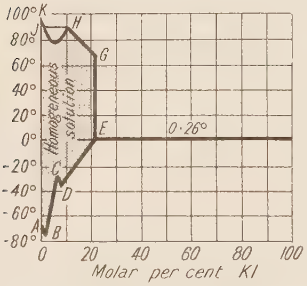


Fig. 151.—The Binary System: $KI–SO_2$.

of the soln., but no sign of the sulphuryliodide, $KI.SO_2$, was observed. Comparison of the f.p. of aq. soln. containing both sulphur dioxide and potassium iodide (or thiocyanate) with those of soln. of sulphur dioxide and potassium iodide (or thiocyanate) separately shows that there are probably compounds formed which, however, are dissociated to a large extent. Further, in agreement with C. J. J. Fox's results, sulphur dioxide is more soluble in aq. soln. of potassium chloride, bromide, iodide, and thiocyanate, rubidium and tetramethylammonium iodides, and resorcinol than in pure water; in sodium chloride soln., sulphur dioxide is less soluble. F. Ephraim and I. Kornblum also made red potassium tetrasulphuryl iodide, as well as lemon-yellow **rubidium tetrasulphuryliodide,** $RbI.4SO_2$, melting at 13·5°, and canary-yellow **cæsium tetrasulphuryliodide,** $CsI.4SO_2$. They also obtained orange-red **barium tetrasulphuryldiiodide,** $BaI_2.4SO_2$, yellowish-red **barium disulphuryldiiodide,** $BaI_2.2SO_2$; red **strontium disulphuryldiiodide,** $SrI_2.2SO_2$, and **strontium tetrasulphuryldiiodide,** $SrI_2.4SO_2$, while red **calcium tetrasulphuryldiiodide,** $CaI_2.4SO_2$, tends to decompose with the liberation of iodine. The aluminium halides also unite with a mol of sulphur dioxide at low temp. A. Adrianowsky observed the formation of a complex **aluminium sulphuryltrichloride,** $AlCl_3.SO_2$, *i.e.* $Cl_2 : Al.SO_2.Cl$, by the action of the gas on aluminium trichloride—*vide infra*, potassium cyanide.

F. Ephraim and C. Aellig observed that a yellow colour is developed when sulphur dioxide is passed into soln. of ammonia, potassium or sodium hydroxide, alkali carbonates, sulphites, hydrosulphites, formates, acetates, and to a less degree a soln. of calcium hydroxide or zinc acetate; but not in soln. of alkali chlorides, nitrates, sulphates, hydrosulphates, alkaline earth (excepting calcium), hydroxides or carbonates, magnesium or cadmium hydroxides, or free sulphuric acid. The colour does not appear when the dilution exceeds 0·5N-soln., and is a maximum in 5N-soln. where it is quite stable. Its absorption spectrum is very like that of a chromate soln. of the same tint. The soln. do not follow Beer's law on dilution, thus indicating that a compound is formed. A compound could not be isolated, but its composition is not far from that of a hydrosulphite.

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CHAPTER LVIII

SELENIUM

§ 1. The History and Occurrence of Selenium

In 1817, J. J. Berzelius[1] said that the sulphuric acid works at Gripsholm roasted the copper pyrites from Fahlun to obtain the necessary sulphur dioxide, and it had been noticed for a long time that a red, pulverulent substance collected on the floors of the lead chambers, but not when other sources of sulphur were employed. He gave the following account of the discovery of a new element in this deposit:

> In conjunction with J. G. Gahn, I was examining the method formerly in use at Gripsholm for preparing sulphuric acid. We found in that acid a sediment, partly red and partly light brown, which, when heated before the blowpipe flame, gave an odour like that of rotten radishes, and left a grain of lead. That odour had previously been assumed by M. H. Klaproth to indicate the presence of tellurium, and J. G. Gahn remembered that he had often noticed the smell of tellurium in places where the copper ore of Fahlun was worked for the sulphur employed in the manufacture of the sulphuric acid. The hope of discovering such a rare metal induced me to examine this brown sediment. In undertaking this research, my only object was to separate the tellurium, but I was unable to detect that body in the material I examined. I therefore had the whole of the sulphuric acid deposits collected, using nothing but that derived from the Fahlun sulphur. Having obtained a large quantity of the material, I examined it in detail, and so discovered the presence of an unknown substance with properties closely resembling those of tellurium. This resemblance induced me to call the new element **selenium**, from the Greek word σελήνη, which signifies the moon, while *tellus* is the name of our own planet.

During the subsequent years, J. J. Berzelius examined in some detail the chemical properties of selenium and its compounds. It might be added that near the beginning of the fourteenth century, Arnold de Villanova, in his *Rosarius philosophorum*, spoke of a *sulphur rubeum* attached to the walls of the chambers in which native sulphur had been vaporized; and F. Hoefer[2] asked: *Serait-ce le sélénium?*

S. Piesse[3] discussed some relations between the elements based on isomorphism and thought that selenium is an oxide of another element; but the speculations were abortive. A. Pringle made a wholesale discovery of new elements including five metals and a substance resembling selenium, called *hesperisium*, in some Lower Silurian rocks, situated in the county of Selkirk. One metal was said to be like iron, but gave neither the thiocyanate nor the tannic acid reaction; one was like lead in appearance, was easily fused and volatilized, and yielded yellow and green salts; another, which was charcoal-black, was called *erebodium*; its equivalent was 95·4, and it formed several oxides. A fourth, *gadenium*, with an equivalent of about 43·6, was a light-grey powder, and formed a red monoxide and a cream-coloured dioxide, yielding, respectively, white and yellow salts. Another, *polymnestum*, was a rather dark-coloured metal, with an equivalent of about 74. Not one of these discoveries has been confirmed.

Selenium is widely distributed on the earth's crust, but occurs only in small quantities. F. W. Clarke and H. S. Washington[4] estimated that it occurs in igneous rocks in quantities about the same as silver, and more than platinum. They estimate that the igneous rocks contain $n \times 10^{-8}$ per cent. of selenium; and J. H. L. Vogt, $n \times 10^{-9}$ per cent. W. Vernadsky gave $0{\cdot}0_5 1$ for the percentage amount, and $0{\cdot}0_5 5$ for the atomic proportion. H. A. Rowland,[5] and M. N. Saha failed to detect the lines of selenium in the solar spectrum; but H. N. Warren detected extra-terrestrial selenium to the extent of 0·04 to 0·23 per cent. in meteoric irons which fell at Bohumilitz, Pallus, Elbogen, and in the Actacama Desert.

According to C. Hintze,[6] the evidence for the occurrence of free selenium in nature is *vollkommen werthlos.* In 1888, A. M. del Rio reported that he obtained from Culebras, Mexico, a red mineral which he supposed was a biseleniuret of zinc coloured with " bisulphuret of mercury or cinnabar," and a grey mineral supposed to be " a biseleniuret of zinc united to a protosulphuret of mercury." H. J. Brooke called the red mineral *culebrite*—from Culebras—and the grey mineral, *riolite*—after A. M. del Rio. In a note to H. J. Brooke, A. M. del Rio said that " riolite is not a seleniuret of zinc but rather a native selenium ore with a variable mixture of sulphoseleniuret of mercury and seleniurets of cadmium and iron." More or less garbled descriptions of these minerals were repeated in subsequent mineralogical works ; and the statements are cited but not confirmed in C. F. de Landero's work on the mineralogy of Mexico. F. Stromeyer, E. Quercigh, W. Haidinger, and L. Bombicci discussed the selenium admixed with the sulphur of the Lipari Islands ; and J. D. Dana, and G. V. Brown, the seleniferous sulphur of Kilauea, Sandwich Islands. According to E. Divers, the sulphur of Japan is seleniferous and telluriferous. R. V. Matteucci and E. Giustiniani observed selenium in the fumarole products during the eruption of Vesuvius in 1895 ; and F. Zambonini and L. Coniglio also observed selenium and tellurium on Vesuvius. The *selentellurium* from Honduras is, according to E. S. Dana and H. L. Wells, the nearest approach to native selenium which has yet been found. It has 29·31 per cent. of selenium and 70·69 per cent. of tellurium. G. Frebold discussed the paragenesis of selenium ores.

There is a number of rare selenide minerals analogous with the sulphides—for instance, **berzelianite,** Cu_2Se, of H. Rose, and C. M. Kersten ; **umangite,** Cu_3Se_2, of F. Klockmann ; **naumannite,** $(Ag_2,Pb)Se$, of H. Rose ; **tiemannite,** HgSe, of C. M. Marx ; **eucairite,** $(Cu,Ag)_2Se$, of J. J. Berzelius, and I. Domeyko ; **clausthalite,** PbSe, of J. K. L. Zincken, and H. Rose ; **lerbachite,** PbSe with HgSe, of H. Rose, the 3PbSe.HgSe, of C. F. Rammelsberg ; **seebachite,** $2PbSe.4CuSe.Cu_2Se.HgSe$; **zorgite,** PbSe with Cu_2Se, of H. Rose and C. M. Kersten ; **crookesite,** $(Cu,Tl,Ag)_2Se$, of A. E. Nordenskjöld ; **aguilarite,** $Ag_2(S,Se)$, of F. A. Genth ; **guanajuatite, castillite,** or **frenzelite,** Bi_2Se_3, of V. Fernandez, A. del Castello, A. Frenzel, and J. D. Dana ; **joseite,** $Bi_3Te(S,Se)$, by G. A. Kenngott, and A. Damour ; **sialonite,** Be_8Se_3, or Bi_3Se, by V. Fernandez and S. Navia ; **weibullite,** $2PbS.Bi_4Se_3S_3$, of M. Weibull, and G. Flink ; **platynite,** $PbS.Bi_2Se_2$, of G. Flink ; **wittite,** $5PbS.3Bi_2(S,Se)_3$, of K. Johannson, and A. Schwandte ; **rubiesite,** $8Bi_2S_3.Sb_2S_3.Bi_2(Te,Se)_3$, of S. P. de Rubies, and C. Doelter ; **onofrite,** Hg(S,Se), of H. Rose, and C. M. Kersten ; and the lead cobalt selenide of F. Stromeyer. There is also the **selenolite,** SeO_2, of E. Bertrand ; the hydrated copper selenite, **chalcomenite,** $CuSeO_3.2H_2O$, of A. des Cloizeaux and A. Damour ; the **molybdomenite,** or lead selenite, of E. Bertrand ; **cobaltomenite,** probably cobalt selenite, of E. Bertrand ; the copper lead cobalt selenide, **penroseite** of S. A. Gordon ; and **kerstenite,** or lead selenite (or selenate), of C. M. Kersten.

Selenium occurs in small proportions in some minerals, etc. For example, it has been observed by J. J. Berzelius, L. Gmelin, C. M. Kersten, J. A. von Lewenau, G. Lunge, H. von Meyer, C. Müller, T. Nordström, A. Pleischl, A. Scheuer-Kestner and A. Rosenstiehl, B. Scholz, E. P. Thomson, F. Wöhler, L. Wolkoff, etc., in various forms of pyrites ; and when the pyrites is employed as a source of sulphur in the manufacture of sulphuric acid (*q.v.*), the products are contaminated with selenium although a large proportion appears as a slime in the lead chambers, and as dust in the flues. The presence of selenium in sulphuric acid was discussed by A. Jouve, P. Kienlen, J. G. Children, A. Scheuer-Kestner, E. Moles and S. Pina de Rubies, E. P. Thomson, G. Lunge, A. Lamy, M. P. Sergéeff, N. A. Orloff, F. Schlagdenhauffen and C. Pagel, and T. W. Drinkwater ; while S. Littmann studied the mode of formation of selenium and its compounds in the burning of pyrites, and in the manufacture of sulphuric acid. Selenium may also occur in derived products ; thus, H. N. Warren noticed it in nitric acid ; and T. Bayley, and W. B. Hart discussed the yellow colour of hydrochloric acid, the latter of whom attributed it to selenium. E. Moles and S. Pina de Rubies found selenium in hydrochloric acid; F. Schlagdenhauffen and C. Pagel observed that the violet-blue colour observed when an impure hydrogen flame is allowed to impinge on a cold surface is due to the presence of selenium, and not to sulphur. A large proportion of the selenium originally present in the materials from which the gas was prepared remains in the insoluble black residue, and F. W. Tunnicliffe and O. Rosenheim found it in brewing sugar, and beer.

H. W. Turner, and J. M. Curran reported selenium in gold ores; W. Steinkhuler, in uraninite; F. J. Otto, in copper pyrites; and W. Geilmann and H. Rose, in the lead and mercury ores of St. Andreasburg in the Harz. R. Böttger, and R. Kemper observed it in the other copper ores; and, in consequence, selenium may appear in the undefined copper as observed by H. Rössler, C. Alexi, H. Violette, G. W. Lehmann and co-workers, and E. Kellar—*vide infra*, cuprous selenide. J. H. Debray, H. Violette, and L. Opificius found selenium in silver. J. J. Berzelius and P. P. Pilipenko observed selenium in galena; J. M. Curran, in bismuth ores; C. M. Kersten, in pitchblende, and cuprite; C. Bödeker, in pseudo-malachite; A. Pleisch, and M. Guichard, in molybdenite; J. J. Berzelius, B. Scholz, A. Wehrle, W. Muthmann and E. Schröder, F. A. Genth, in tellurium ores; A. Jorissen, in coal from Liége; and J. F. Smith, A. Damour, and A. Frenzel, in coke from Yorkshire. F. Taboury noted that the soluble matter in the mineral waters of La Roche-Posay contains 0·2 per cent. of selenium. Arsenic had previously been reported in these waters, but that element is absent, showing that the ore was mistaken for the other. T. Gassmann detected hydrogen selenide in rain-water and in snow. He said that it is probable that hydrogen selenide is not present as such in the rain or snow, but is in combination with a second component which has not yet been identified. P. Karrer denied this.

According to T. Gassmann,[7] selenium is a constant constituent of teeth and bones. He said that healthy teeth contain about 0·056 per cent. of selenium, and even the diseased condition about the same figures for the selenium content are obtained. The urine contains 0·0011 per cent. of selenium in the male, and 0·0009 per cent. in the female person. Most vegetables contain traces of selenium, especially spinach. On the other hand, R. Fritsch denied the presence of selenium in urine or in bones.

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§ 2. The Extraction and Purification of Selenium

J. J. Berzelius[1] obtained selenium from the chamber slimes of the sulphuric acid works by dissolving the material in aqua regia, and evaporating the soln. with sulphuric acid so as to precipitate the lead sulphate. The filtrate was treated with hydrogen sulphide so as to precipitate the copper, mercury, tin, arsenic, and selenium sulphides ; the precipitate was digested with aqua regia, and the clear liquid was evaporated to drive off the excess of acid, and then mixed with a little alkali-lye so as to precipitate the oxides of the heavy metals. The alkaline filtrate was evaporated to dryness, and heated to redness to drive off any mercury. The product, containing alkali selenite, was mixed with ammonium chloride and heated in a retort until the ammonium chloride had all volatilized. The ammonia reduces the selenite to selenium. The residue was washed with water; the selenium collected by filtration, dried, and purified by sublimation. K. Liebe used a somewhat similar process. Instead of reducing selenium from alkali selenite by ammonium chloride, J. A. von Lewenau precipitated it directly from the soln. by ammonium sulphite. F. Wöhler used sulphurous acid as precipitant for selenium, and also substituted for aqua regia a mixture of sulphuric acid and nitric acid or potassium chlorate; he also fused the material with a mixture of potassium nitrate and carbonate; dissolved the cold cake in hydrochloric acid, and precipitated the selenium by a current of sulphur dioxide. W. Stahl extracted the selenium from the slime by means of fuming sulphuric acid, or persulphuric acid, and afterwards precipitated the selenium by sulphur dioxide. Z. Littman modified the process. L. M. Dennis and J. P. Koller fused smelter flue-dust with a mixture of 300 grms. of flue-dust, 200 grms. of anhydrous sodium carbonate, and 775 grms. of sodium dioxide in a large nickel crucible until the mass melted quietly. After cooling, the product was treated with water and insoluble material filtered off; it was then nearly neutralized with hydrochloric acid, which precipitated most of the zinc and aluminium. After filtration, a large vol. of hydrochloric acid was added, and the soln. boiled for thirty minutes to reduce the selenic acid to selenious acid; any silica present was precipitated at this stage; the filtrate was then heated to 80° and treated with sodium sulphite in small quantities. The selenium separates, and is converted into the grey modification by digesting it with the soln. for several hours at 80°. J. A. von Lewenau, and B. Scholz treated the slime repeatedly with nitric acid in what was equivalent to a flask with a reflux condenser. The soln. was evaporated to dryness, extracted with boiling water, the filtered liquid concentrated by evaporation, and the selenium precipitated with ammonium sulphite. L. M. Dennis and J. P. Koller obtained selenium from anode slimes containing 96 per cent. Se, by adding the slime to conc. nitric acid to which one-fifth of its volume of water had been added; a vigorous action ensued, and when this had moderated, the mixture was heated to complete the oxidation. The soln. was filtered, and a viscous, dark green liquid obtained which was evaporated to dryness. The residue was taken up with hydrochloric acid (3 : 1) and the selenium precipitated by sulphur dioxide or sodium sulphite.

H. Rose extracted the selenium by heating the dried deposit in a current of dry chlorine so that the deposit does not fuse. The vapours of selenium and sulphur chlorides are received in a vessel containing water, and the filtered liquid treated with alkali sulphite to precipitate the selenium. C. Brunner passed a current of air over the heated deposit so as to convert the sulphur into sulphur dioxide, at the same time the selenium sublimes as oxide which is dissolved in alkali-lye, etc. G. Magnus heated the material with manganese oxide, and obtained the same volatile products as C. Brunner obtained with air. H. Koch mixed the chamber deposit into a paste with moderately conc. sulphuric acid, and stirred it up with dry potassium permanganate at 50°–60°. The reaction: $4KMnO_4+5Se+6H_2SO_4=2K_2SO_4+4MnSO_4+5SeO_2+6H_2O$ is complete when the solid becomes white and the acid liquor red. Sodium chloride is then added to precipitate any silver which may be present and the mixture is diluted and filtered, the selenium being precipitated from the acidified filtrate by means of sulphurous acid. About 80 per cent. of the total selenium may thus be isolated. O. Pettersson treated the deposit with a conc. soln. of potassium cyanide, and decomposed the soln. of selenocyanate with hydrochloric acid, etc. L. F. Nilson used a similar process, but purified the product by transforming it into selenium dioxide, and after sublimation, dissolving the selenium dioxide in acid, and precipitating the selenium with sulphur dioxide. M. Shimose recommended the potassium cyanide method for separating selenium when tellurium is also present, and separated the tellurium by A. Oppenheim's process. H. Schnitzler, A. von Schrötter, and E. Priwoznik, etc., also discussed the separation of selenium from telluriferous minerals—*vide infra,* tellurium. R. Threlfall separated the mixed oxides by repeated sublimation in a current of dust-free, dry air at 300°. R. Böttger treated the washed slime with a conc., neutral, aq. soln. of sodium sulphite until the slime begins to blacken, the soln. was filtered into dil. hydrochloric acid, and the treatment repeated on the separated selenium. If a boiling soln. of sodium sulphite is used, the selenium does not dissolve. S. Sugie, and T. Shiomi and K. Ozu discussed this subject.

P. Kienlen suspended the deposit in water and passed a current of chlorine so as to form selenium tetrachloride which is at once hydrolyzed by water to selenium dioxide and some is oxidized by the excess of chlorine to selenic acid. This is reduced to selenious acid by boiling hydrochloric acid, and at the same time selenium chloride is formed. This is decomposed by a sulphite. He also obtained selenium from the acid from Glover's tower in a sulphuric acid works by allowing the liquid dil. with three times its vol. of water, to stand in a warm place for some time. The selenium gradually settles. J. Personne treated the dil. acid with sulphur dioxide so as to precipitate the selenium. J. R. Joss freed the precipitated selenium from calcium sulphate by washing it with boiling water. H. Bornträger heated the deposit to redness in an earthen retort in the absence of air, and found that the selenium sublimed. It was well washed with alkali-lye and then with water so as to remove the arsenic and selenium oxides.

A. Wehrle fused potassium hydroxide with seleniferous galena, sulphur, or pyrites, digested the fused mass with water, and exposed the filtered soln. to air when the selenium was precipitated. F. Wöhler extracted selenium from lead selenide minerals by digesting the powdered ore with dil. hydrochloric acid to remove iron and calcium carbonates; the washed and dried residue was fused with an equal weight of black flux in a charcoal crucible for an hour at a moderate heat. The powdered mass was quickly washed with boiling, air-free water so long as the runnings exhibited any colour. If the selenide of potassium in the liquid comes in contact with air, selenium is precipitated. The reddish-brown filtrate is exposed to air in shallow dishes, and the crusts which are formed are broken up from time to time. The formation of these crusts continues until the liquid becomes colourless, and the traces of selenium still present can be removed by warming the liquid with hydrochloric and sulphurous acids. The crusts of selenium are washed and freed by distillation from a little admixed selenide. E. Mitscherlich fused the powdered material with an equal weight of sodium nitrate; extracted the product with boiling water; and evaporated by boiling with a little nitric acid. The hot liquid deposits crystals of sodium selenate; on cooling, sodium nitrate separates out; and the mother-liquor when concentrated again deposits sodium selenate. The sodium selenate is mixed with ammonium chloride, and heated. The mass which remains is washed with water and selenium remains. L. Billaudot obtained 37 kgrms. of selenium from 139·5 kgrms. of zorgite by treating it with aqua regia; evaporating the liquid at a gentle heat; filtering off the lead chloride; and passing sulphur dioxide through the soln. The precipitated selenium was washed with water, to free it from copper chloride, boiled with hydrochloric acid to free it from lead chloride, and finally washed with water, dried, and melted. Great difficulty was experienced in obtaining bars of vitreous selenium. When it was cast in cast-iron moulds, the cooling was so slow that the graphite modification was obtained. By casting in copper moulds with thin walls, plates of vitreous selenium 0·5 cm. thick were obtained, but the best results were obtained by placing the mould in water, and pouring in the melted selenium when it had cooled nearly to the solidifying point; it then immediately solidified in the vitreous modification. A bar 3 cms. thick, and weighing 12·6 kgrms., was thus obtained. M. Chikashige and D. Uno obtained selenium and the noble metals from electrolytic slimes, etc., by fusion. The electrolytic slime or other product is fused with lead and a suitable alkali in the form of hydroxide, carbonate, or nitrate, the noble metals being obtained as an alloy with lead and the selenium in combination with the alkali metals.

H. Rose observed that selenium is imperfectly precipitated by sulphur dioxide in the presence of sulphuric acid alone, but E. Divers and M. Shimose showed that this refers only to dil. sulphuric acid, for precipitation is complete if the acid be sufficiently concentrated. D. L. Ogden and R. E. Valentine also used sulphur dioxide, free from hydrogen chloride, as a precipitant for selenium. For other precipitants, *vide infra*, the analytical reactions of selenium; and also the action of metals on selenious acid. H. Rose, and A. Oppenheim have discussed the purification of tellurium (*q.v.*) from traces of selenium. Selenium can be separated from all metals not precipitated by sulphurous acid and arsenic, antimony, and tin. The completeness of the precipitation of selenium depends on the acidity of the soln. E. Keller found that the precipitation of selenium and tellurium by sulphur dioxide shows characteristic differences. The graphs, Figs. 1 and 2, refer to cold soln. containing 0·10 grm. of selenium or tellurium treated by sulphur dioxide in presence of different proportions of hydrochloric acid (sp. gr. 1·175). The curves indicate the amounts of these elements precipitated on standing about 20 hrs. With soln. containing over 80 per cent. of hydrochloric acid, all the selenium and no tellurium is precipitated. Consequently, to obtain both elements completely precipitated, not less than 30 or over 50 per cent. of acid should be present. If selenium alone be present, total precipitation occurs if the acidity of the soln. exceeds 30 per cent.; if both selenium and tellurium be present, tellurium and selenium will be precipitated if the acidity of the soln. be kept between 30 and 50 per cent.; but outside these limits either selenium or tellurium may be wholly or partially precipitated, according to the conc. of the acid. Selenium will alone be precipitated from a mixed soln. if the acidity of the soln. exceeds 80 per cent. Hence, if selenium be first precipitated from a soln. of over 80 per cent. acidity, and made up to twice its former vol. with water, the tellurium will be precipitated by a repetition of the sulphur dioxide treatment. C. Alexi also found that with 1, 5, 10, and 50 c.c. of hydrochloric acid of sp. gr. 1·124, 10 c.c. of a soln. with 0·1 grm. selenium, dil. to 100 c.c., sulphur dioxide precipitated respectively 0·0543, 0·0986, 0·0993, and 0·0973 grm. of selenium; with similar soln. having 10 c.c. of the acid, at 19°, 50°–60°, 70°–80°, and 90°-100° the amounts precipitated were respectively 0·0993, 0·0998, 0·0992, and 1·014 grm.

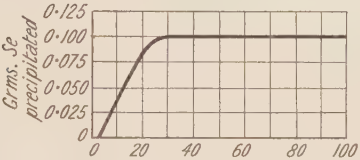

FIG. 1.—Influence of Acidity of Solution on the Precipitation of Selenium.

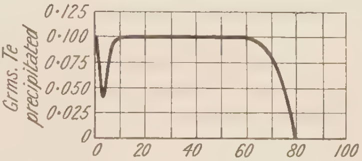

FIG. 2.—Influence of Acidity of Solution on the Precipitation of Tellurium.

A. Garnak did not get good results in separating selenium from sulphuric acid residues by the sulphite process, and he recommended adding gradually, with energetic stirring, 600 grms. conc. sulphuric acid to a kilogram of deposit (3·5 per cent. of selenium); 140 grms. of manganese dioxide is gradually introduced into the mixture at 90° to 95°. After 2·5° to 3 hrs., the selenious acid is extracted with 3 litres of water. The united soln. are then treated with 10 grms. of hydrochloric acid, and 120 grms. of sodium thiosulphate, and the selenium is coagulated by boiling the soln., washed with 200 c.c. of hot water, and dried at 50°. The yield is 90 per cent.

F. C. Brown recommended freeing the selenium from occluded gases by heating it in a high vacuum, and subliming the element. E. Divers and M. Shimose purified selenium by dissolving it with boiling conc. sulphuric acid; diluting the soln.

with water; precipitating the selenium with sulphur dioxide; washing the precipitate with water, then with alcohol; and drying it in air. C. Hugot digested the crude selenium with dil. nitric acid; evaporated the mixture to dryness; sublimed the resulting selenium dioxide; dissolved the product in water and removed a trace of sulphuric acid by the addition of a little baryta-water; acidified the filtrate with hydrochloric acid, and precipitated the selenium with sulphur dioxide. R. Marc used a somewhat similar process. E. Divers and T. Shimidzu said that hydrogen selenide in excess with sulphurous acid gives a precipitate of pure selenium. L. T. Brownmiller stated that the selenium on the market contains traces of dioxide, which appears under the miscroscope as opaque particles when selenium is used as a medium for the determination of indices of refraction. To prepare selenium optically clear, it suffices to distil the element in an atm. of carbon dioxide.

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§ 3. The Allotropic Forms of Selenium

Selenium, like sulphur, furnishes a number of allotropic forms. J. J. Berzelius[1] recognized a non-crystalline variety which when warmed softens before it melts; a red amorphous variety which was obtained by reducing selenium dioxide; a steel-grey, crystalline variety obtained by slowly cooling molten selenium; and a black crystalline variety produced by the spontaneous decomposition of a selenide exposed to air. F. von Schaffgotsch, J. W. Hittorf, and E. Mitscherlich showed that the steel-grey and black crystalline varieties are the same. The two amorphous varieties are said to be soluble in carbon disulphide, and the crystalline varieties soluble and insoluble respectively. From his own and F. Neumann's observations on the sp. gr., C. F. Rammelsberg assumed that there are four varieties: (i) red, amorphous selenium of sp. gr. 4·3, and soluble in carbon disulphide; (ii) red crystalline selenium of sp. gr. 4·46–4·50, and soluble in carbon disulphide; (iii) grey, granular, metallic selenium of sp. gr. 4·5, and insoluble in carbon disulphide; and (iv) black selenium of sp. gr. 4·8 and insoluble in carbon disulphide—it is obtained by the spontaneous decomposition of aq. soln. of selenides in air. The two red forms pass into grey metallic selenium at 90°–100°; and all the varieties when melted and rapidly cooled pass into the red, amorphous form. E. Petersen considered that both forms insoluble in carbon disulphide are really the same. He called the amorphous variety soluble in carbon disulphide—*α-selenium*; the monoclinic variety soluble in carbon disulphide—*β-selenium*; and the other crystalline variety insoluble in carbon disulphide—*γ-selenium.* W. Muthmann showed that there are really three crystalline forms—two monoclinic varieties, and a rhombohedral or trigonal variety. They were studied by E. Korinth, who found the evaporation of a soln. of red, amorphous selenium in carbon disulphide furnishes small, hexagonal, yellowish to reddish-brown, transparent, birefringent, crystals with extinction parallel to the longer side of the hexagon. The crystals are monoclinic and are isomorphous with η-sulphur. If these crystals are added to a soln. of sulphur, the sulphur is deposited on the selenium crystals as an isomorphous layer. If only a little soln. of selenium is added to one of sulphur, the η-form of sulphur is produced almost exclusively, but the crystals of sulphur, under high magnification, appear to contain tiny particles of selenium embedded in the sulphur. H. O. Schulze also established the existence of colloidal selenium. From this, A. P. Saunders, and W. Muthmann concluded that there are three allotropic forms of selenium: (i) The *glassy* or *vitreous*, the *amorphous*, and the *colloidal* forms soluble in carbon disulphide; (ii) red monoclinic crystals soluble in carbon disulphide, of which there are two varieties with different axial ratios, one of which forms isomorphous mixtures with sulphur, and the other does not; and (iii) grey metallic or trigonal selenium isomorphous with tellurium, and insoluble in carbon disulphide. Summarizing:

Se
- Soluble in CS_2
  - liquid, amorphous, vitreous, glassy, or colloidal.
  - red monoclinic crystals
    - isomorphous with sulphur.
    - not isomorphous with sulphur.
- Insoluble in CS_2-grey, metallic, trigonal crystals.

Liquid selenium above 220° has properties characteristic of ordinary liquids; below that temp., the liquid becomes more and more viscous, but it remains soft down to about 60°, and, at 30°–40°, it becomes hard and brittle. This behaviour is characteristic of vitreous glasses and undissolved or congealed liquids in the co-called amorphous state—Fig. 11, **1**. 9, 6. J. J. Berzelius, J. W. Hittorf, H. V. Regnault, A. P. Saunders, E. Petersen, and E. Ruhmer studied the formation of undissolved selenium. In this undissolved state, selenium has the conchoidal brilliant fracture characteristic of glasses, and is the so-called **glassy selenium** or the **vitreous selenium** of commerce. Formerly this selenium was marketed in medallions having the image of J. J. Berzelius, the discoverer of the element, but it is now usually supplied in the form of rods. The colour *en masse* is black, but thin fragments are deep ruby-red in transmitted light, and it furnishes a red powder. The so-called **amorphous selenium** separates out when soln. of selenious acid are reduced. According to A. P. Saunders, it forms a dry impalpable powder without any signs of crystallization. At 40°–50°, it darkens in colour, and coagulates to a soft mass which, when cooled, becomes a hard and brittle mass with a conchoidal fracture. Allowing for differences in the state of aggregation, amorphous selenium shows all the characteristics of vitreous selenium. Both amorphous and vitreous selenium are slightly soluble in carbon disulphide. J. W. Hittorf, and H. V. Regnault also discussed the identity of amorphous and vitreous selenium. G. Briegleb found that the X-radiograms showed the presence of two components, Se and Se_2, which have the same solubility in carbon disulphide, but different rates of solution in that menstruum.

F. W. O. de Coninck found that a sulphuric acid soln. of selenium, reduced by glucose from selenious acid, slowly decomposes: $SeSO_3+H_2O=Se+H_2SO_4$, yielding a brown variety of selenium which does not become fluorescent when exposed to diffused light, or undergo any change in contact with carbon disulphide, in which it is very sparingly soluble. On prolonged exposure to sunlight, it is slowly converted into the amorphous black variety of selenium. F. W. O. de Coninck and A. Raynaud found that the selenium precipitated when a moderately conc. soln. of selenious acid is treated with a sat. soln. of sulphur dioxide, after exposure to diffused daylight, is partly transformed into grey crystalline leaflets having a fine lustre; the remainder undergoes a slight agglomeration, but does not change colour and remains amorphous. The former change is visibly enhanced by sunlight. Two varieties of selenium are supposed to be involved.

In accord with W. Ostwald, A. P. Saunders showed that amorphous selenium separates by preference in all cases where selenium is rapidly set free either by decomposing one of its compounds, or by precipitation from soln. of its vapours. As observed by H. Rose, and A. Oppenheim, amorphous selenium is produced when selenium is dissolved in potassium cyanide and precipitated by hydrochloric acid; J. J. Berzelius, when selenious acid is reduced by sulphur dioxide, or by zinc or iron; J. W. Hittorf, by stannous chloride; H. Rose, by phosphorous acid; A. P. Saunders, by ferrous or chromous chloride or by hydrogen—A. Klages observed an emission of light when selenium dioxide is reduced by hydrogen; W. F. O. de Coninck and E. Chauvenet reduced the soln. of selenium dioxide by glucose, aldehyde, and other organic substances—*vide infra;* G. Magnus, R. Auerbach, and J. W. Hittorf, by adding water to soln. of selenium in conc. sulphuric acid—*vide infra;* B. Rathke, by decomposing selenothionates by acids; or selenium chloride by water; R. Schneider, by decomposing selenium bromide with alcohol; P. Jannasch and M. Müller, by reduction with hydrazine sulphate or hydroxylamine hydrochloride; J. W. Hittorf, by slowly oxidizing hydrogen selenide by air, or, according to C. Fabre, with ferric chloride, selenium dioxide, or hydrogen dioxide; H. Uelsmann, by decomposing various selenium compounds—*e.g.* potassium selenide; M. Berthelot, by the electrolysis of aq. soln. of hydrogen selenide; S. Bidwell, in the electrolysis of soln. of selenious acid, or by passing a current through a selenium cell; L. Schucht, by the electrolysis of acidic or alkaline soln. of selenium; and H. Bornträger, by subliming the element whereby the amorphous form condenses in the cooler parts of the tube—some grey selenium is formed at the same time. M. G. Weber made the variety soluble in carbon disulphide by abruptly cooling the vapour as in the method of H. Erdmann and M. von Unruh for yellow arsenic (*q.v.*). A. Gutbier and R. Köhler passed the vapour of selenium into water free from air. The soln. are usually rose-coloured, and at first blue and cloudy; sometimes they are clear yellowish-red or deep red. The yellowish-red soln. are the most highly dispersed. They all show the Brownian movement, and the Tyndall effect. The blue soln. are quite stable, and may be kept in closed vessels for months at ordinary temp.; non-dialyzed soln. may be frozen to an almost colourless ice; when thawed they quickly decompose.

When, say, 5 per cent. soln. of selenious acid and sulphurous acid are mixed there is no precipitation at first, the colour in transmitted light then changes from yellow, through reddish-yellow, and yellowish-red, to a more or less deep blood-red, and only after the lapse of a certain time is a deposit of red selenium formed. This makes its appearance as a golden-yellow or a red translucent skin upon the sides of the containing vessel. H. O. Schulze, working with very dil. soln. of selenious and sulphurous acids ($SeO_2 : SO_2=1 : 2$), obtained soln. of **colloidal selenium** as a *hydrosol.* The colouring power of selenium in the colloidal state is very marked; a soln. with one part of selenium in 10,000 parts of water has a distinct red tinge. P. I. Cholodny prepared colloidal soln. in a similar way. S. Utzino, and H. Paulson prepared colloidal selenium by grinding in the colloid mill. The red precipitate is peptized or deflocculated if an excess of water be added, but if the precipitate is aged or if it has been exposed to light, its deflocculation may not occur so readily. The colloidal soln. is stable in the dark, but when exposed to light, the selenium may be deposited as a red film or skin. All foreign soluble substances may be removed by dialysis. The colloidal soln. may be boiled without decomposition, but the selenium is salted out by the addition of salts or acids. W. Biltz also prepared colloidal soln. of selenium by reducing selenious acid with sulphurous acid; J. Meyer used soln. of hyposulphites as reducing agent—A. Gutbier and R. Emslander prepared *alcosols* in a similar way; A. Gutbier and co-workers, with titanous chloride; and A. Gutbier, hydrazine hydrate (1 : 2000) and 0·2 per cent. soln. of selenious acid, and also hydroxylamine hydrate or phosphorous acid; R. Auerbach obtained colloidal soln. of selenium in pyrosulphuric acid—*vide infra*, action of that acid on selenium. J. Meyer dissolved selenium in a conc. soln. of hydrazine hydrate, and dil. the liquid. A. Gutbier and F. Heinrich studied the results obtained with sodium or ammonium hydrosulphite, sulphurous acid, sodium hyposulphite, and hydrazine salts. A. Gutbier and F. Engeroff obtained colloidal soln. by the hydrolysis of various selenium bromides; J. Meyer, by the action of dil. sulphuric acid on sodium selenosulphate; P. P. von Weimarn and B. V. Maljisheff, by adding a soln. of selenium in carbon disulphide to ether; and A. Pochettino obtained sols in a variety of indifferent solvents, retene, fluorene, phenanthrene, anthracene, naphthalene, α-naphthol, α-naphthylamine, diphenylmethane, diphenylamine, triphenylamine, phenol, thymol, and paraffin. The solvent is heated to about its b.p. (above the m.p. of selenium) in presence of selenium, the liquid assuming an increasingly dark red coloration. When solidified, the soln. appears red by reflected, and blue by transmitted light, this double coloration being characteristic of colloidal suspensions of selenium with large particles. These soln. can be repeatedly solidified and liquefied without alteration of their properties. A. Gutbier and G. L. Weise obtained the colloid by the electrolysis and dialysis of aq. soln. of selenium dioxide. E. Müller and R. Nowakowsky prepared a colloidal soln. by the electrical pulverization in pure water of a cathode prepared by fusing a small piece of selenium on to platinum foil. This takes several hours with an e.m.f. of 20 volts, or is effected more quickly with a greater e.m.f. The hydrogen selenide formed with an e.m.f. of 20 volts is oxidized by the anodic and atmospheric oxygen; but with an e.m.f. of 220 volts, hydrogen selenide is evolved. The colloidal soln. is fiery yellowish-red in thick layers, or a dirty yellow in thin layers, by transmitted, or yellowish-red by reflected light, and deposits selenium only slowly, except on the addition of an electrolyte. A. Pochettino also prepared colloidal soln. by electrical pulverization; H. Neugebauer, by mechanical trituration in a soln. of lactose; and S. Utzino observed that the maximum stability of the soln. does not necessarily occur with the finest state of subdivision. S. Roginsky and A. Schalnikoff obtained the colloid by distilling selenium, and collecting the vapour on a surface cooled by liquid air. F. Ehrenhaft and G. Wasser discussed the aerosols of selenium. F. W. O. de Coninck and E. Chauvenet used for the reduction glucose, or other organic reducing agents—levulose, formaldehyde, paraldedehyde, benzaldehyde, formic acid, oxalic acid, malonic acid, venanthol, etc. C. Paal and C. Koch prepared soluble colloidal selenium in a solid form by using sodium protalbate or lysalbate as protective colloid. They said that the liquid hydrosol of selenium is obtained by reducing selenious acid, dissolved in aq. sodium protalbate or lysalbate, with hydrazine hydrate and hydrochloric acid, or with hydroxylamine hydrochloride, and dissolving the precipitate so obtained in aq. sodium carbonate. The liquid hydrosol, after purification by dialysis, is blood-red by reflected light, or, when strongly diluted, red by transmitted light. The solid hydrosol, obtained in dark red, glistening flakes when the soln. is evaporated by gentle heat and finally over sulphuric acid, contains 32 to 50 per cent. of selenium, and is easily soluble in cold water. This form is much more stable than the hydrosols previously obtained; in aq. soln., it remains unchanged on repeated alternate treatment with acetic acid and sodium hydroxide, or when boiled with an excess of 10 per cent., sodium chloride or phosphate soln., but is gelatinized on addition of an excess of calcium chloride soln. in the cold. A specimen of this solid hydrosol, after preservation for 2½ years, dissolved almost completely in water. Colloidal selenium, containing up to 90 per cent. of selenium, is obtained by dissolving the solid hydrosol in water and adding acetic acid as long as precipitation takes place. The Chemische Fabrik von Heyden used white-of-egg, or analogous substances, as protective colloid; L. Lilienfeld used proteins, gum arabic, or gelatine; D. L. Shrivastava and co-workers, sugars; R. Ditmar, caoutchouc; A. Gutbier and R. Emslander, gelatin; A. Gutbier, J. Huber and P. Eckert, extract of seeds of *Plantago psyllium;* A. Gutbier and U. Rhein, saponin; A. Gutbier, extract of carob beans; A. Gutbier found that relatively stable sols of selenium may be prepared by evaporating on the water-bath, to a syrupy consistency, an aq. soln. containing equimolecular quantities of selenium dioxide and dextrose, and then adding one drop at a time of conc. ammonia, taking care that the soln. remains syrupy. After cooling and mixing with water, reddish-brown sols are obtained which after a short time are stable, and contain about 0·016 grm. of selenium per 100 c.c. The stability of the sol is increased by the presence of a slight excess of dextrose. The sols are stable on boiling, but on freezing they are completely and irreversibly coagulated if there is no excess of dextrose. The sols are sensitive to electrolytes. **Glycerol sols** can be prepared in the same way as the hydrosol and have similar properties.

P. I. Cholodny found the sp. gr. of colloidal selenium to be 4·26 to 4·27 at 0°/4° in agreement with the value for amorphous selenium. A. Gutbier and co-workers found that when the colloidal soln. is frozen, and melted, most of the selenium returns into soln. If the freezing is repeated many times, or if the sol is kept in the frozen condition too long, the colour by transmitted light becomes less intense and the stability of the sol becomes much less, particularly toward an increase in temp. The nature of the reducing agent employed in the preparation of the sols and the temp. of preparation have a great influence on the stability toward freezing. R. Auerbach obtained colloidal soln. of selenium in pyrosulphuric acid—*vide infra,* action of that acid on selenium. H. R. Kruyt and P. C. van der Willigen, H. R. Kruyt and D. R. Briggs, and K. von der Grinten studied the cataphoresis of colloidal selenium. The flocculation of colloidal soln. of selenium by acids, and salts was examined by H. O. Schulze, A. Gutbier and co-workers, J. Meyer, P. C. L. Thorne and co-workers, P. I. Cholodny, H. R. Kruyt and co-workers, and J. J. Doolan. S. Utzino observed that the stability of colloidal soln. of selenium decreases with increasing dispersion of the particles. A soln. with particles of average size 52$\mu\mu$ could be kept for a year. J. J. Doolan, A. Gutbier and R. Köhler, and W. Biltz found that colloidal selenium migrates to the anode. A colloidal soln. of selenium gives a precipitate with colloidal hydroxides of iron, aluminium, chromium, cerium, and zirconium, and selenium is adsorbed from its colloidal soln. by silk. A. Gutbier and B. Ottenstein obtained a purple colour by depositing the colloid on stannic hydroxide. W. Reinders discussed the distribution of the colloid between two solvents; and S. Kwartin, the Brownian movement in gases.

E. Mitscherlich obtained red or dark maroon crystals of **monoclinic selenium** by slowly cooling a hot soln. of selenium in carbon disulphide. He observed that selenium separates from carbon disulphide in monoclinic crystals in two different habits—as thin, transparent, red leaflets; and as grains so intensely coloured as to appear opaque and almost black although thin fragments have the same colour as the leaflets. He obtained the largest crystals by subjecting amorphous selenium and carbon disulphide in a sealed tube, to successive changes of temp. somewhat below 100°. W. Muthmann observed that two monoclinic forms separate from carbon disulphide soln. The two types have different degrees of stability, and different axial ratios—one—**α-monoclinic selenium**—in orange-red having $a:b:c=1{\cdot}63495:1:1{\cdot}6095$, and $\beta=75°\ 38'$; the other—**β-monoclinic selenium**—having $a:b:c=1{\cdot}5916:1:1{\cdot}1352$, and $\beta=86°\ 56'$; the latter usually occurs in short, thick prisms, but sometimes it occurs in leaflets easily confused with the former crystals. A. P. Saunders found that when benzene is added to a soln. of selenium in carbon disulphide, a crop of minute, pale-red plates is soon deposited. M. L. Frankenheim obtained what he called oblique rhombic prisms from a soln. of selenium in conc. sulphuric acid ; A. P. Saunders obtained metallic selenium in a similar manner. The red monoclinic form was also prepared by E. Petersén, and W. Muthmann.

The direct change of vitreous to the red monoclinic crystalline form has not been observed with certainty. Since metallic selenium melts at about 217°, the red monoclinic forms are unstable and should have a m.p. below that temp. E. Mitscherlich said that the red, monoclinic crystals melt if rapidly heated to 200°, but this may mean that the heat developed when the vitreous form passes into metallic form may be great enough to raise the temp. of the selenium to its m.p. The observed m.p. thus represents a special case of what A. P. Saunders calls *self-fusion.* A. P. Saunders heated mixtures of selenium with an inert organic substance, and found that the selenium could be fused below 205°, whereas crystals of gallein acetate, m.p. 205°, did not fuse. He therefore inferred that red monoclinic selenium has an unstable m.p. at 170°–180°. When the monoclinic crystals are triturated, they furnish a red powder which is indistinguishable from the red powder of amorphous selenium. E. Mitscherlich said that they are stable at 100°, but at 150° pass into the metallic form. C. F. Rammelsberg said that the crystals are not stable at 100°, but W. Muthmann placed the **transition temperature** of the one form of monoclinic crystals at 110°–120°, and of the second at 125°–130°. The second monoclinic form is stable at 110°. J. J. Berzelius, etc., observed that when any of the forms of selenium, just indicated, is heated above 217°, **metallic selenium** is produced in hexagonal-rhombohedral crystals which, according to W. Muthmann, are isomorphous with the trigonal crystals of tellurium. This is the stable form of the element. It looks like a steel-grey, metallic substance, which furnishes a black powder, but if the powder be very fine, it appears red. B. Rathke said that the powder is always black, but E. Mitscherlich observed that the finest powder is red.

M. L. Frankenheim obtained what he called oblique, rhombic prisms by sublimation ; J. Fröbel, rhombic prisms by exposing an aq. soln. of ammonium selenate in air. The acute crystals obtained by A. Pleischl, by sublimation, were suspected by J. J. Berzelius to be mercury selenide. H. Bornträger, and W. Muthmann prepared the crystals by sublimation. J. W. Hittorf, E. Mitscherlich, B. Rathke, and C. F. Rammelsberg obtained this form of selenium by the action of air on aq. soln. of potassium or sodium selenide ; and J. J. Berzelius, and J. Fröbel, from aq. soln. of ammonium selenide. C. Fabre said that selenium separates in the metallic form when hydrogen selenide is decomposed by moist oxygen ; A. Ditte, by the thermal decomposition of hydrogen selenide in sealed tubes ; and M. Berthelot, by the electrolysis of selenious acid. The metallic selenium collects on the cathode and is partly soluble and partly insoluble in carbon disulphide. E. Petersen said that the black, metallic selenium obtained by the electrolytic process contains about 0·5 per cent. of soluble selenium ; and the best metallic selenium he obtained from the vitreous form contained about one per cent. of the soluble form.

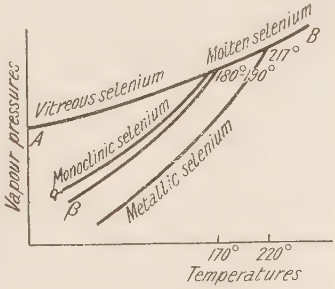

Fig. 3.—Vapour Pressure Curves of the Different Forms of Selenium (Diagrammatic).

As indicated above, metallic selenium melts at about 217°, and monoclinic selenium probably between 170° and 180°. The diagrammatic curves of the relation between the vapour pressures of the different forms of selenium and temp. are illustrated by A. P. Saunders by Fig. 3. The state of vitreous selenium is illustrated by the curve *AB.*

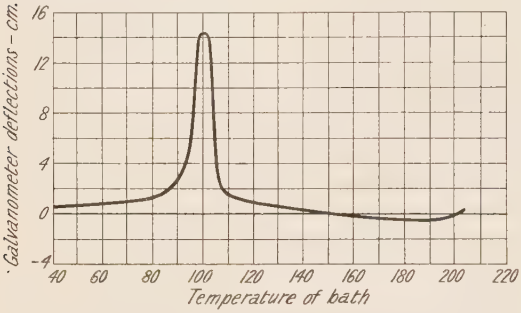

Fig. 4.—Showing the Temperature of Selenium when Heated in a Bath at Different Temperatures.

There is no definite m.p. F. Sacc said that while metallic selenium melts at 217°, the vitreous form only becomes liquid at 240° to 250°. As shown by A. P. Saunders, the same liquid is obtained at 217° with all varieties of selenium. The liquid at that temp. has a moderately high viscosity, and when cooled under ordinary conditions it furnishes the vitreous form, but if the cooling be very slow, the metallic form appears. The conversion of the vitreous to the metallic form was shown by H. V. Regnault to be attended by the evolution of much heat, so that when the vitreous form is gradually heated, there is a sudden rise in temp. from about 96° to about 150°, when the mass becomes a mobile fluid, but it hardens again in a few minutes. The product is metallic selenium. This explains how J. J. Berzelius could say that the vitreous form becomes semi-fluid at 100° and completely so a few degrees higher. R. Marc measured the difference of temp. between the bath and the selenium with the bath at different temp., and the results are plotted in Fig. 4. H. V. Regnault's temp. 96° does not represent a transition point. The change does not possess a measurable velocity below 90°; W. Hittorf said that it may occur anywhere between 80° and 217°; and C. F. Rammelsberg gave 90° as the limit of stability; and above 95° the change goes on rapidly. J. W. Hittorf said that the maximum velocity of the transformation occurs at about 125°. The idea of a transition temp. in the conversion of vitreous to metallic selenium was accepted by G. Tammann; and H. le Chatelier could say, "selenium is only stable in the crystalline state above 60° and below 214°. Outside of these extreme limits of temp., the amorphous modification alone is stable," probably owing to the following observation by O. Lehmann:

> When melted under a cover-glass, selenium appears as a clear red transparent liquid; on further warming, the liquid gets darker and black points make their appearance here and there; these increase in size and assume the aspect of spherical aggregates of the insoluble grey modification. . . . The crystals soon fill the whole field, and, on still further heating, the mass melts to a dark, almost opaque liquid. On cooling down slowly, the spherical crystals of the grey modification appear at first, and then, as they grow steadily smaller, the colour of the liquid becomes less intense, and we obtain finally the original clear red liquid. If the cooling is rapid, the crystals of the grey modification do not appear, but the liquid passes gradually from dark red to light red. The same behaviour is shown on rapid warming; here also the black crystals may appear momentarily and disappear again, but sometimes the transition is direct from the red condition into the more deeply coloured one. The increased absorption of light on heating and the reverse change on cooling, point to a chemical change in the liquid such that it is to be regarded at higher temp. as partially a soln. of the grey modification. On attempting later to reproduce the above inversion it did not prove possible to do so; perhaps because of greater or less impurity of the selenium, perhaps because the conditions were not favourable for the production of the grey (light-sensitive, less conducting) modification.

A. P. Saunders could not verify this. He made a number of dilatometric measurements with vitreous selenium at different temp., and in the presence of various liquids he found no evidence of any stable form other than metallic selenium with a sp. gr. 4·8. The metallic form is stable throughout its range up to nearly 200°, whereas the vitreous form passed into the metallic form at any temp. ranging from 60° to 80° according to the liquid present; only one form of selenium can exist permanently at 200°. It makes no difference whether fused selenium be cooled to 200°, or whether vitreous selenium be rapidly heated to 200°, or again, whether it be allowed to go over at any lower temp. and then raised to that point—the final sp. gr. at 200°

is always the same and lies along the sp. gr. curve for metallic selenium. Sunlight causes no change of vol. in metallic selenium either at ordinary temp. or at higher ones, up to 200°. It is not as a rule possible to raise the temp. of vitreous selenium above about 140° without a sudden change into the metallic form, but it may occasionally, by rapid heating, be brought to 180° or above before the change takes place. When metallic selenium is kept at ordinary temp. or placed in a bath heated to 40°, 50°, or 60°, or any higher temp., below 220°, it shows no tendency to go over into any other form.

A. P. Saunders observed that when amorphous selenium is heated with various substances, the results can be broadly arranged in three groups: (i) Those which have little or no action—*e.g.* water, hydroxylamine hydrochloride, hydroxylamine, urea, ammonium sulphocyanate, picric acid, acetanilide, potassium hydroxide, ammonium chloride, and potassium ferrocyanide; (ii) Those which transform it into red monoclinic selenium—*e.g.* alcohol, benzene, thiophene, toluene, benzonitrile, propyl aldehyde, amyl nitrite, ethyl acetate, isobutyric acid, acetophenone, nitrotoluene, bromonitrobenzene, dinitrobenzene (*m*), dimethylaniline, nitroso-β-naphthol, acetone, propylene bromide, ethyl iodide, mono-methyl aniline, chloroform, phenyl hydrazine, benzylamine, and diphenylmethane; and (iii) Those which transform it into metallic selenium—*e.g.* quinoline, aniline, pyridine, benzyl cyanide, benzimidobutyl-ester, piperidine, triethylamine, hexamethyleneamine, and *p*-β-anisaldoxime. The substances which are most active in bringing about the change to the metallic form will be seen to be ring compounds containing nitrogen in the ring; these without exception all show the same behaviour. All the substances which cause this change are nitrogen compounds, but not by any means all nitrogen compounds are capable of causing the change; thus, while aniline acts rapidly in transforming amorphous selenium into metallic, both mono- and di-methyl-aniline change it into the red crystalline form. This makes it appear as if solubility alone is not sufficient to account for the differences in the behaviour of the liquids.

R. Marc supposed that metallic selenium really consists of two modifications: one is a non-conductor of electricity, while the other is an electrical conductor. The former he called selenium-A, and the latter selenium-B. When the B-form is heated above 210°, it is transformed into the A-variety; and when the A-form is cooled to —40°, it is converted into the B-form. The A-form is stable above 70°, and the B-form below 8°. At ordinary temp., the A-form passes slowly into the B-form, and this change is accelerated by white or red light, but retarded by blue light. G. Briegleb's X-radiograms, however, showed that R. Marc's conducting and non-conducting varieties are the same. According to R. Marc, the variety produced by heating amorphous selenium forms grey crystals; it is labile and is converted into a more stable form at a rate which, above 170°, can be measured by the development of heat. The transition of the labile into the more stable form may also be followed by the gradual increase of the electrical conductivity during the transition. The latter form, however, does not appear to be the most stable variety of selenium. When the labile form is quickly cooled, the conductivity rapidly increases until at the ordinary temp. the value is 1000–2000 times as great as initially; on remaining at the ordinary temp., however, this variety of selenium decreases steadily in conductivity. The most stable form of selenium exists probably between 217° and 160°, when a condition of equilibrium between two modifications is attained; whether those modifications are the forms described or two other forms is uncertain. Whilst amorphous selenium in thin layers has a red tint, the labile crystalline form is grey with a faint red tint and the more stable crystalline form is bluish-grey. Whilst the amorphous form is exceedingly brittle, the labile crystalline form is less so and the more stable crystalline form is malleable. Traces of impurities in selenium have a great influence in retarding its crystallization. Selenium-A and -B form equilibrium mixtures such that in the dark the equilibrium mixture consists almost exclusively of A, and the equilibrium is displaced in the direction of B by raising the temp. The transition has been observed microscopically, the round granular crystals of *A* first formed at 140° changing to the longer crystals of *B* when heated for some time at 200°. Further, *B* appears to be rather less soluble in carbon disulphide than the other modification. The equilibrium mixture at the ordinary temp. is sensitive to light, but when heated at 200° for some time (so that practically only *B* is present) and then rapidly cooled, this is no longer the case; however, when kept at the ordinary temp., it becomes more and more sensitive as the equilibrium becomes displaced in the direction of *A*. It is therefore considered that light displaces the equilibrium from *A* to *B*, as does rise of temp. The effect in question is really photochemical and not due to simultaneous heating, and the sensitiveness is the same in dry air, in carbon dioxide, and in a vacuum. Owing to the very slight transparency of selenium, only an extremely thin layer is affected by light, but there is some evidence that the particles thus affected diffuse slowly towards the interior, a fresh layer being thus exposed. E. Berger said that a comparison of the electrical conductivity of selenium—*vide infra*—quenched from different temp. favours the hypothesis of a compound Se_{AB}, which forms solid soln. with both components. Hence, the f.p. curves and the conductivity curves of the two forms are illustrated diagrammatically in Fig. 5, where the quenching temp. are inferred to the assumed proportions of Se_A and Se_B, which are supposed to be formed. According to H. R. Kruyt, metallic selenium which has not been heated above 120° has a sp. gr. 4·5 to 4·6, while sublimed selenium has a sp. gr. 4·80. The difference is not due to the presence of amorphous selenium. After fusion, and crystallization at 125°, the sp. gr. is 4·77; the variety of sp. gr. 4·80 also acquires a sp. gr. 4·77 at 125°. Hence, the case of selenium-A and -B is one of dynamic allotropy $Se_A \rightleftharpoons Se_B$, where a high temp. favours the denser form. The insolation of selenium produces an increase in vol. showing that illumination favours the production of selenium-A. The changes in electrical conductivity (*q.v.*) are explained on the assumption that the two forms yield solid soln. The anomalous behaviour of selenium cooled from 200° is attributed to the combined action of light and heat altering the equilibrium, and changing the speed at which equilibrium is attained. All phases of selenium are supposed to contain selenium-A and -B, whilst red, crystalline selenium is labile and may also occur in two modifications. C. Ries did not accept H. R. Kruyt's conclusions. H. Pélabon said that the electrical resistance of metallic selenium may vary from a few ohms to several million ohms, and he assumes that it consists of two modifications. The α-modification has a very high resistance and is prepared by heating selenium at a temp. only just above its m.p. and then allowing it to cool slowly. The specific resistance of this modification diminishes at first very rapidly with rise in temp. and then more slowly. At 200°, the resistance is about 70,000 ohms, and at 218° the substance melts, the melting being accompanied by a sudden rise in resistance. The β-modification has a very small specific resistance. It is obtained by maintaining the molten selenium at a temp. near its b.p. for some time and then allowing it to cool. The β-modification is not stable at low temp., and it is readily changed into the α-form by oscillations of its temp. between 15° and 200°. This hypothesis recalled the suggestion of C. F. Rammelsberg that there are two modifications of metallic selenium—one with a sp. gr. 4·5 he called *körniges*, and the other with a sp. gr. 4·8, *blättriges*. A. P. Saunders, however, could not verify this; nor was E. Petersen able to distinguish two forms of metallic selenium.

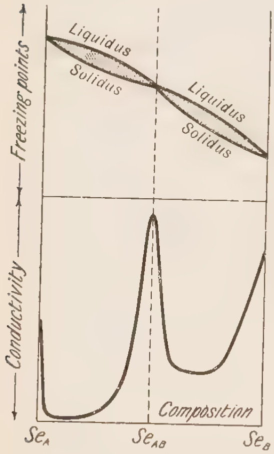

FIG. 5.—Freezing-point, and Electrical Conductivity Curves of Selenium quenched from Different Temperatures.

The close relationship between sulphur and selenium has naturally stimulated attempts to correlate the allotropic forms of these two elements. J. J. Berzelius compared red selenium with monoclinic sulphur, metallic selenium with rhombic sulphur, and plastic sulphur, metallic selenium with rhombic sulphur, and plastic sulphur with vitreous selenium. M. Berthelot compared red monoclinic selenium with rhombic sulphur, and amorphous sulphur with metallic selenium because of their behaviour towards carbon disulphide and because on electrolyzing an aq. soln. of hydrogen selenide, red selenium is deposited on the anode, while an aq. soln. of selenic acid under similar conditions gives metallic selenium on the cathode—*vide* sulphur. E. Mitscherlich correlated red selenium to rhombic sulphur, and metallic selenium to monoclinic sulphur. B. Rathke compared metallic selenium with rhombic sulphur, amorphous red selenium with amorphous sulphur insoluble in carbon disulphide, and red monoclinic selenium with monoclinic sulphur. E. Petersen suggested that rhombic sulphur corresponds with metallic selenium insoluble in carbon disulphide; monoclinic sulphur with monoclinic selenium; amorphous, insoluble sulphur with amorphous, red selenium; and plastic sulphur with vitreous selenium. These guesses are based on superficial analogies. C. F. Rammelsberg sought to establish a crystallographic relationship between W. Muthmann's monoclinic sulphur-II with the α-monoclinic selenium. By suitably orienting the crystals he obtained for the axial ratios of the former $a:b:c=0{\cdot}99:1:1{\cdot}27$, and $\beta=89^\circ\ 15'$, and for the latter, $0{\cdot}99:1:1{\cdot}00$, and $\beta=84^\circ\ 14'$. A. Bettendorff and G. vom Rath showed that the crystal forms of sulphur and selenium as well as those of their compounds are very different. W. Muthmann said that the two elements are not isomorphous, but it is possible that α-monoclinic selenium is isomorphous with W. Muthmann's IV-sulphur, where the axial ratios are respectively $a:b:c=1{\cdot}6349:1:1{\cdot}6095$, and $\beta=104^\circ\ 2'$, and $1{\cdot}5925:1:1{\cdot}5567$, and $\beta=105^\circ\ 29'$. Mixed crystals with 68·5 per cent. of selenium and 31·5 per cent. of sulphur were obtained of this form from carbon disulphide soln. The β-monoclinic selenium does not correspond with any of the forms of sulphur, although if the axial ratios be alone considered, and those of β-monoclinic selenium be multiplied by two-thirds, then γ-sulphur has the axial ratios $a:b:c=0{\cdot}06094:1:0{\cdot}70944$, and $\beta=88^\circ\ 13'$, and β-monoclinic sulphur $0{\cdot}0611:1:0{\cdot}7658$, and $\beta=86^\circ\ 56'$. Mixed crystals with 48 per cent. of selenium and 52 per cent. of sulphur were obtained of this form from carbon disulphide soln. W. Muthmann also assumed that metallic selenium may correspond with the so-called black sulphur (*q.v.*). The tendency to crystallize in the metallic form increases in the series: S, Se, Te, with increasing at. wt. This form of tellurium is the only one known; with selenium this is the stable form at ordinary temp. and above 130°; and this form with sulphur is very difficult to obtain. V. M. Goldschmidt discussed the crystal structure of selenium.

According to L. Angel,[2] if vitreous selenium melted at 220° is cooled rapidly under press. it is transformed into a new variety, violet-grey in appearance, formed of slender crystals, very sensitive photoelectrically, but very unstable.

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§ 4. The Physical Properties of Selenium

The colour of selenium has been discussed in connection with the allotropic states of the element. By circulating a stream of selenium in carbon disulphide, S. Kyropoulos[1] obtained crystals 2 mm. long which were ruby-red by transmitted light and had a blue metallic heating by reflected light. A. H. Pfund found that thin layers, obtained by cathodic spluttering, are greyish-brown in transmitted light, and lead-grey in reflected light. According to J. J. Berzelius, the vapour of selenium is a darker yellow than chlorine, and paler than sulphur vapour; it condenses in narrow vessels to drops with a metallic lustre: in wide vessels, to red *flowers of selenium*; and in air, to a red cloud. W. Grippenberg said that when selenium is cooled between glass-plates, the surface appears smooth, but it is not so. There are many small pits due to crystals whose major axis is perpendicular to the plate. Hence an electrode does not make perfect contact with such a selenium plate. L. P. Sieg found that spluttered films are crystalline. The red **crystals** of the monoclinic form were discussed by E. Mitscherlich. W. Muthmann

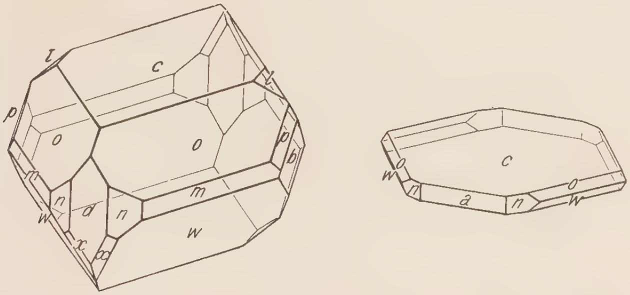


Fig. 6.—Crystals of α-monoclinic Selenium.

found that the crystals of α-monoclinic selenium have the axial ratios $a:b:c=1{\cdot}63495:1:1{\cdot}6095$, and $\beta=104°\ 2'$, the measured crystals had the forms illustrated by Fig. 6. The crystals of β-monoclinic selenium have the axial ratios

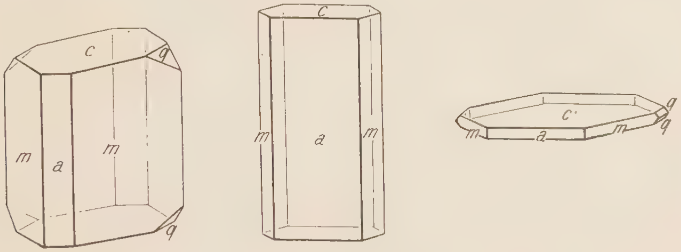


Fig. 7.—Crystals of β-monoclinic Selenium.

$a:b:c=1{\cdot}5916:1:1{\cdot}1352$, and $\beta=93°\ 4'$. Those which were measured had the forms illustrated by Fig. 7. The trigonal crystals of metallic selenium had the form illustrated by Fig. 8, and C. Ries said that the crystals are isomorphous with tellurium. M. K. Slattery found the axial ratios to be $a:c=1:1{\cdot}14$. F. C. Brown obtained crystals of metallic selenium in rhombohedral or hexagonal shapes; other crystals grew in clusters of spines or needles which were stiff and tough; while other crystals consisted of flexible plates 0·01 mm. thick. They were obtained by distilling selenium at various temp., and under various press. The plates were obtained when the temp. was low. G. Pellini and G. Vio, and J. F. Norris and R. Mommers discussed the isomorphism of selenium and tellurium compounds; J. W. Retgers, and W. E. Ringer, the isomorphism of sulphur and selenium; and the general subject, by E. C. Schröder. A. J. Bradley said that the **X-radiograms** show that the crystals of trigonal selenium may be regarded as simple rhombohedral structures with interaxial angles of almost 90° in which each atom is slightly displaced towards two of the six adjacent atoms. The resulting structure is a threefold spiral compound of three interpenetrating simple triangular lattices—*vide* the case with tellurium. M. K. Slattery, however, said that the crystals have a simple, triangular lattice with three atoms associated with each point of the lattice. The side a of the basal triangle is 4·34 A.; S. von Olshausen gave $a=4{\cdot}379$ A. The data were summarized by P. P. Ewald and C. Hermann. M. K. Slattery found

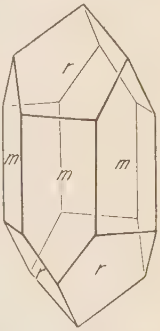


Fig. 8.—Trigonal Crystal of Metallic Selenium.

the axial ratios $a:c$ to be 1 : 1·14; and the calculated density 4·84; S. von Olshausen gave 4·838.

The **vapour density** of selenium was found by H. St. C. Deville and L. Troost [2] to be 7·67 at 860°; 6·37 at 1040°; and 5·63 at 1420°—theoretical value for Se_2 is 5·5 so that it consists of diatomic molecules at about 1400°. H. Biltz gave 5·54 at 1750° to 1800°. From his investigations of the vap. density of arsenic selenide, E. C. Szarvasy assumed that some Se_2-molecules are present at 900°–950°. H. von Wartenberg found that the vap. density at 1850° agreed with a mol. wt. of 200°, and at 2100°, with a mol. wt. of 120 so that there is a perceptible dissociation: $Se_2 \rightleftharpoons 2Se$ at about 2000°. G. Preuner and J. Brockmöller showed that the vap. densities agree with the assumption that up to about 900°, the mols. of selenium are chiefly Se_6 and Se_2 with a small proportion of monatomic selenium; at temp. lower than 550°, the molecules are probably Se_8. W. Vaubel made observations on this subject; and he calculated from the b.p. of selenium that the molecules of the liquid are triatomic, Se_3; while E. Beckmann calculated from the effect on the f.p. of phosphorus that the molecules are octatomic, Se_8. E. Beckmann and P. Geib found that the effect of selenium on the f.p. of sulphur monochloride agrees with the assumption that the molecules of selenium in that solvent are monatomic—the soln. is dark red. E. Beckmann obtained from the f.p. of soln. of selenium in iodine, Se to Se_8, whereas in diphenyl and in anthraquinone, the mol. wt. is eq. to Se_8; and E. Beckman and C. Platzmann, in iodine in the presence of sulphur, as Se_2. F. Olivari from the effect on the f.p. of iodine obtained a mol. wt. Se_{10} at 4°—*vide infra,* selenium iodides—owing to the formation of iodides. E. Paterno thought F. Olivari's result valueless. R. Hanslian observed that an iodide is formed, and he obtained rather less than the value for $Se_2=158·4$ for the mol. wt. calculated from the effect of selenium on the f.p. and the b.p. of iodine. For E. Beckmann and C. Platzmann's observations with soln. of selenium in iodine, *vide* selenium iodide —and in sulphur, *vide* selenium sulphide. R. Auerbach's cryoscopic observations showed that in pyrosulphuric acid, selenium dissolves as Se-mols. E. Beckmann found that in chlorine and bromine, the formation of halides prevents a determination of the mol. wt. in these solvents. With soln. of selenium in mercuric chloride, F. Olivari's observation on the f.p. agreed with the mol. Se_3 and Se_4 increasing with increasing conc. to Se_8. Observations were also made with mercuric bromide. The f.p. of soln. in anthraquinone or phenanthraquinone agrees with Se_3 to Se_4 for dil. soln., and Se_8 in conc. soln. R. Auerbach found that in soln. of pyrosulphuric acid, selenium is present as diatomic molecules, but above 130°, as monatomic molecules—*vide infra,* oxysulphates. V. Kistiakowsky studied the mol. constitution of liquids, and inferred that selenium is polymerized in the liquid and gaseous states.

J. J. Berzelius [3] gave 4·30 to 4·32 for the **specific gravity** of vitreous selenium; F. von Schaffgotsch, 4·276 to 4·286—mean 4·281 at 20°; C. F. Rammelsberg, 4·29 to 4·36—mean 4·30; P. Boullay, 4·310; G. Quincke, 4·20; M. Coste, 4·302 at 17°; P. I. Cholodny, 4·278 at 0°/4°; E. Petersen, 4·29; and A. P. Saunders, 4·28. For the so-called red amorphous selenium, F. von Schaffgotsch gave 4·245 to 4·275—mean 4·259 at 20°; and for a sample which had been heated under water at 50° until it had turned greyish-black, 4·250 to 4·277—mean 4·264. C. F. Rammelsberg gave 4·27 to 4·34—mean 4·30; P. I. Cholodny, 4·28 at 0°/4°; B. Rathke, 4·26 to 4·28; and A. P. Saunders, 4·26 at 25°. For colloidal selenium. P. I. Cholodny gave 4·26 at 0°/4°. For the sp. gr. of red monoclinic selenium, E. Mitscherlich gave 4·46 to 4·509 at 15°, and after turning grey at 150°, 4·7, C. F. Rammelsberg gave 4·51; E. Petersen, 4·46; P. I. Cholodny, 4·44 at 0°/4°; and A. P. Saunders, 4·44 to 4·47 at 25°. For metallic selenium obtained from aq. soln. of alkali selenides W. Hittorf gave 4·808 at 15°; E. Mitscherlich, 4·760 to 4·788 at 15°; C. F. Rammelsberg and A. P. Saunders, 4·8 at 15°; and E. Petersen, 4·78; and for metallic selenium obtained by heating the vitreous form, F. von Schaffgotsch gave 4·796 to 4·805—mean 4·801 at 20°; A. Bettendorff and

A. Wüllner, 4·797 at 20° ; F. Neumann, 4·40 ; C. F. Rammelsberg, 4·5 ; E. Petersen, 4·63 ; P. I. Cholodny, 4·78 at 0°/4° ; B. Rathke gave 4·80 to 4·81 ; and A. P. Saunders, 4·8 at 25°. M. Toepler found the vol. expansion on fusion is 0·018 c.c. per gram. M. Coste gave 4·302 for the sp. gr. of sticks of fused selenium at 17°, and after conversion into the metallic form, 4·356 ; but the product contained cavities, and after repeated crushing and boiling in toluene, the sp. gr. was 4·80 ; and the long needles obtained by crystallization on cooling from 230° a soln. of selenium in a conc. soln. of potassium hydroxide, 4·82. H. R. Kruyt gave 4·80 for sublimed selenium, and 4·5 to 4·6 for grey crystalline selenium which had not been heated above 120°. Both forms have a sp. gr. 4·77 after being heated to 125° for some time. The specifically lighter variety is selenium-A, and the specifically heavier variety selenium-B, while 4·77 represents the sp. gr. of a sample of both forms in dynamic equilibrium $Se_A \rightleftharpoons Se_B$. W. Spring gave for metallic selenium before and after compression at 600 atm. press. :

	0°	20°	40°	60°	80°	100°
Uncompressed .	4·7312	4·7176	4·7010	4·6826	4·6623	4·6396
Compressed . .	4·7994	4·7869	4·7699	4·7526	4·7351	4·7167

A. P. Saunders gave for the best representative values of the three forms of selenium : 4·27 for vitreous and amorphous selenium ; 4·47 for red monoclinic selenium ; and 4·80 for metallic selenium. The corresponding **atomic volumes** are respectively, 18·55, 17·72, and 16·50. Some theoretical observations on this subject were made by E. Donath and J. Mayrhofer, C. del Fresno, I. I. Saslawsky, and J. A. Groshans. H. Schröder discussed the vol. relations of the sulphates, selenates, and chromates ; and F. Hund, those of the selenium ion. W. L. Bragg calculated for the **atomic radius** 1·17 A. ; L. S. Ransdell, 1·15 A. ; A. Ferrari, 2·25 A. ; W. F. de Jong and H. W. V. Willems, 1·13 A. ; E. N. Gapon, 1·28 A. ; and M. L. Huggins, 2·24 A. V. M. Goldschmidt, L. Pauling, E. T. Wherry, and H. G. Grimm made observations on the ionic radius from which it follows that for sexivalent selenium, the effective at. radius is 0·42 A. : for neutral atoms, 1·13 to 1·17 ; and for bivalent negative atoms, 1·91 to 1·98 A. J. Geissler found the ionic vol. of Se″ to be 3·293. J. R. Rydberg [4] gave 2·0 for the **hardness** of selenium on Mohs' scale. C. Schäfer gave 0·45 for **Poisson's ratio,** that is, the ratio of the lateral contraction to the longitudinal extension when stretched longitudinally. L. P. Sieg and R. F. Miller measured the coeff. of rigidity of single crystals of selenium and found $0{\cdot}64\times10^{11}$ dynes per sq. cm. ; and for Young's modulus, $5{\cdot}8\times10^{11}$ dynes per sq. cm. T. W. Richards gave for the average **compressibility** at 20° between 100 and 500 megabars, 0·000012—*vide* tellurium. I. A. Balinkin discussed the elastic stresses in a plate of selenium. G. Quincke's measurements show that at 217°, the **surface tension** of selenium is 92·5 dynes per cm., and the **specific cohesion** $a^2=4{\cdot}41$ sq. mm.

H. Fizeau [5] found the linear coeff. of **thermal expansion** of vitreous selenium to be $0{\cdot}0_43792$. W. Spring gave for the cubical coeff. for metallic selenium which had been compressed by 600 atm. press., and uncompressed selenium :

	20°	40°	60°	80°	100°
Uncompressed . .	$0{\cdot}0_31478$	$0{\cdot}0_31635$	$0{\cdot}0_31743$	$0{\cdot}0_31857$	$0{\cdot}0_31981$
Compressed . .	$0{\cdot}0_31307$	$0{\cdot}0_31539$	$0{\cdot}0_31644$	$0{\cdot}0_31803$	$0{\cdot}0_31951$

This gives for the linear coeff. of metallic selenium $0{\cdot}0_44927$ at 20° ; $0{\cdot}0_45810$ at 60° ; and $0{\cdot}0_46604$ at 100°. H. G. Dorsey gave for vitreous selenium $0{\cdot}0_4324$ at −160° ; −120°, $0{\cdot}0_4335$; −80°, $0{\cdot}0_4369$; −40°, $0{\cdot}0_4404$; $0{\cdot}0_4439$ at 0° ; and $0{\cdot}0_43792$ at 50°. W. Grippenberg found that the coeff. of expansion is greatest in the direction of the major axis of the crystals. H. F. Wiebe found that like sulphur, phosphorus, and mercury the relation $D^2c(\theta_b-\theta_m)/A_a=2$ for selenium, when A denotes the at. wt. ; D, the sp. gr. ; a, the coeff. of cubical expansion ; θ_m, the m.p. ; θ_b, the b.p. ; and c, the sp. ht.

J. J. Berzelius [6] found the **thermal conductivity** of vitreous selenium to be small.

According to A. C. Schultz-Sellack, selenium plates, 0·4 and 3·0 mm. thick, allow the passage of respectively 50 and 16 per cent. of heat when exposed to lamplight at 100°, and 36 and 5 per cent. when exposed to the light of a gas-flame. H. V. Regnault observed that metallic selenium is a better thermal conductor than vitreous selenium. According to E. D. Sayce, the thermal conductivity of selenium in darkness varies over a wide range and is affected by the conditions which influence its electrical conductivity, and in the same direction, but in general to a slighter extent. The thermal conductivity of vitreous selenium at 25° lies between 0·000293 and 0·000328. That of metallic selenium at 25° varies from 0·00070 to 0·00183. The value for the metallic form increased in general with the temp. of preparation, but diminished with age. The temp. coeff. is positive. M. Bellati and S. Lussana, and A. Pochettino and G. C. Trabacchi found that the conductivity is increased by illumination. B. Nannei found that the thermal conductivity of metallic selenium is increased by the action of light, but to an extent apparently less than is shown with the electrical conductivity. This effect diminishes as the temp. rises. R. E. Martin observed that a selenium cell which was not sensitive electrically was also not sensitive thermally. The red end of the spectrum is more effective than the shorter wave-lengths. The results show that thermal and electrical conductivities in metals largely depend on the same factors. L. P. Sieg showed that whilst a given source of light increased the electrical conductivity nearly 300 per cent., the same light did not increase the thermal conductivity in any appreciable manner. Considering all possible sources of error, it must certainly have been under five per cent.

H. V. Regnault[7] found the **specific heat** of selenium, free from sulphur, to be 0·08349 to 0·08396—mean 0·08371—between 98° and 112°; and later he gave 0·1031 for vitreous selenium between —19° and 87°; between —27° and 8°, 0·07461; and between —20° and 7°, 0·07468. A. Bettendorff and A. Wüllner observed that the sp. ht. of vitreous selenium, obtained by dropping the molten element into cold water, was 0·0953 between 20° and 38°; 0·1104 between 22° and 53°; and 0·1147 between 20° and 62°. A. P. Saunders attributed these variations to the partial transformation of vitreous into metallic selenium; although H. V. Regnault obtained no change in the thermal capacity when vitreous selenium is changed into the metallic form; and for metallic selenium with 2·25 per cent. of tellurium, he gave 0·07616 between 20° and 98°; 0·07323 between —20° and 7°; and 0·07446 between —16° and 7°. F. Neumann gave 0·0860 for the sp. ht. of metallic selenium; and A. Bettendorff and A. Wüllner obtained 0·095 between 18° and 38°, and 0·113 between 21° and 57°; while they obtained 0·0840 between 22° and 62° for metallic selenium of sp. gr. 4·797 obtained by slowly cooling vitreous selenium; and 0·08399 for metallic selenium obtained by the spontaneous decomposition of alkali selenides in air. Accordingly, he concluded that these two forms of selenium are the same. P. Mondain-Monval found the mean sp. ht. of metallic selenium to be 0·084 between 15° and 217°, and 0·078 between 15° and 75°; of red crystalline selenium, 0·082 between 15° and 75°; of vitreous selenium, 0·106 between 15° and 100°; and of liquid selenium, 0·118 between 217° to 300°. J. Dewar gave 0·0271 to 0·0361 for the sp. ht. of selenium between —196° and —253°; 0·068 between 18° and —188°; and 2·86 and 5·39 for the corresponding **atomic heats**; A. Bettendorff's and A. Wüllner's value for the at. ht. is 6·65 for metallic selenium between 22° and 62°; and for vitreous selenium, 7·52 between 18° and 38°, and 8·95 between 21° and 57°.

The action of heat on the different forms of selenium has been previously discussed. Vitreous selenium, being an undercooled liquid, has no definite **melting point**; it becomes less viscous as the temp. rises. E. Mitscherlich[8] said that monoclinic selenium melts when rapidly heated to 200°; while A. P. Saunders inferred that the m.p. is between 170° and 180°; and H. Coste, at 144°, when heated rapidly before it has time to pass to the metallic form. Metallic selenium was found by W. Hittorf, G. Pellini, and H. N. Draper and R. J. Moss to melt at 217° without a preliminary softening ; and, added A. P. Saunders, all forms of selenium pass into the metallic form in the vicinity of 200°. H. Coste gave 219° for the m.p. ; L. E. Dodd, 217·4° ; W. R. Mott, 217° ; and G. Pellini and R. Sacerdoti, 220°. E. Berger found the m.p. of selenium to be 220·2°, 0·5°. This is supposed to refer to a compound of the two allotropes—Fig. 5. This **transition temperature** has been previously discussed. G. Tammann and W. Jellinghaus discussed the vol. changes in relation to the temp. and press. of vitreous selenium. C. Zengelis found evidence that selenium volatilizes slightly at ordinary temp. E. Berger found that the A-form of metallic selenium melts at a lower temp. than the B-form. H. F. Wiebe studied the relations between the m.p., b.p., coeff. of expansion, sp. ht., and at. wt. of this family of elements ; and H. Carlsohn showed that the m.p. of selenium compounds does not conform to the addition rule. S. Datta observed that sublimation occurs over 170°. G. Preuner and J. Brockmöller found for the **vapour pressure,** p mm.,

	390°	440°	480°	500°	620°	660°	680°	680°	700°	710°
p . .	3·0	11·0	21·0	42·0	313·0	550·0	700·0	760·0	865·0	970·0

J. Jannek gave 0·02415 mm. at 200° and 0·03080 mm. at 230°. L. E. Dodd gave 0·00084 mm. at 193·6° ; 0·0048 mm. at 215·5° ; 0·0055 mm. at 217·4° ; 0·0059 mm. at 219·0° ; 0·0138 mm. at 238·0° ; and he represented the results over this range of temp. by an equation of the form $p=ae^{b/T}$, where T denotes the absolute temp. For temp. from 193·6° to 215·5°, $\log p=16{\cdot}692-7644T^{-1}$, and from 221·0° to 238·2°, $\log p=10{\cdot}733-4722T^{-1}$. The results do not agree with an equation of the type $\log p=a+bT^{-1}-c \log T$. For the solid at the m.p., $dp/dT=1{\cdot}050$ bars or 0·000767 mm. per degree, and for the liquid $dp/dT=0{\cdot}573$ bar or 0·000431 mm. per degree. J. J. Berzelius said that selenium boils below a red-heat, but others place the **boiling point** at a higher temp. ; thus, E. Mitscherlich gave 700° ; C. Barus, 687°–694° ; H. Pélabon, 690° ; W. R. Mott, 688° ; T. Carnelley and W. C. Williams, between 676° and 683° ; H. le Chatelier, 638° ; L. Troost, between 664° and 666° at 760 mm. ; and G. Preuner and J. Brockmöller gave 700° at 865° mm., 688° at 760 mm., and 680° at 700 mm. D. Berthelot said that for a press. p mm. of mercury in proximity to the normal press., $690°+\frac{1}{10}(p-760)°$. A Schuller found that selenium is readily sublimed when heated in vacuo ; and F. Krafft and co-workers distilled selenium at 380° in the vacuum of a cathode light ; and at about 310° at 60 mm. press. R. de Forcrand gave 14·595 Cals. for the **heat of vaporization,** at the b.p. and 4·595 Cals. per mol. for the **heat of fusion.** P. Mondain-Monval gave 16·4 cals. per gram ; and W. Herz, 13·4 cals. per gram for the heat of fusion. J. Tate gave 29·4 cals. per gram at 35° for the heat of vaporization. L. E. Dodd calculated 83·9 cals. per gram for the heat of fusion at the m.p. ; 135·5 cals. per gram for the heat of vaporization at the m.p. to form diatomic mols. ; and 219·4 cals. per gram for the **heat of sublimation** of the solid at the m.p. G. Preuner and J. Brockmöller calculated that the **heat of dissociation :** $Se_6 \rightarrow 3Se_2-55{\cdot}96$ Cals. P. M. Monval found the **heat of transformation** of vitreous to metallic selenium to be 13·5 cal. per gram at 130° ; it increases with rise of temp. and at the m.p., 217°, it becomes identical with the latent heat of fusion 16·4 cals. per gram. The heat of transformation of red crystalline selenium to metallic selenium is 2·2 cals. per gram at 150° ; and of vitreous to liquid selenium, 16·4 cals. per gram. E. Kordes calculated Q cals./T =8·6 for the entropy of metallic selenium and 8·6 for Se_4. G. N. Lewis and co-workers gave 15·6 for the entropy of selenium at 25° ; and B. Bruzs, 18·9 for the **entropy** at the m.p. W. Herz studied the subject.

W. S. Gripenberg[9] found that the **refractive index** of crystalline selenium is 3·5 for sodium light—a value higher than that of any other element. Amorphous selenium has a refractive index from 1·16 to 1·27 times less than that of the crystalline element. J. L. Sirks found the index of refraction of selenium for the *A*-line to be 2·654 ; for the *a*-line, 2·692 ; for the *B*-line, 2·730 ; for the *C*-line, 2·787 ; for the *c*-line, 2·857 ; and for the *D*-line, 2·98 ; and A. C. Becquerel gave 2·6550 for the

B-line. S. Kyropoulos gave for red, crystalline selenium, 2·8 parallel to the chief axis, and 2·3 perpendicular to that axis. Observations were also made by W. Meier, K. Försterling and V. Fréedericksz, A. H. Pfund, E. O. Hulburt, C. H. Skinner, R. F. Miller, and L. P. Sieg. R. W. Wood—*vide infra*—found a maximum in the $\mu\lambda$-course when μ is 3·13. The light of an arc-lamp was reflected successively from six surfaces of selenium, and the image of the crater after the sixth reflection, although faint, was without colour or excess of ultra-violet light. P. M. Nicol gave, at 0°,

λ	6470–4170	5890–5896	8100–21900	4400–4800
Refractive index . .	2·37–3·36	2·75–3·06	3·02–2·59	2·74–3·04
Extinction coeff. . .	0·45–0·90	0·77–1·07	1·18–0·90	1·05–1·27

Rough measures on the near ultra-red gave for the index of refraction 2·6, and an extinction coeff. $<$ 0·1. There was no indication of any relation between the optical properties and the temp. of the transformation to the conducting λ form, nor was there any variation with the duration of the exposure to light, or with the age of the specimen. A. Krebs measured the index of refraction in the ultra-red; and H. W. Edwards, the index for X-rays. The **reflecting power** of selenium is shown by the dotted line, Fig. 10. There is no marked change in the reflecting power between $\lambda=400\mu\mu$ to $1000\mu\mu$, and at $600\mu\mu$ there is a small maximum. These results are in agreement with those of P. G. Nutting who found a maximum at $590\mu\mu$ to $600\mu\mu$, and a slow drop in the reflecting power in the violet, and a rapid fall in the ultra-violet. K. Försterling and V. Fréedericksz observed that the reflecting power is constant between $289\mu\mu$ and $240\mu\mu$, but variable with light of greater wave-lengths. W. W. Coblentz found reflecting power in the ultra-red to be 18·20 per cent. R. W. Wood found for the **reflecting power,** R; the index of refraction, μ; and the **extinction coefficient,** k, for light of wave-length λ.

λ . . .	$0·400\mu$	$0·490\mu$	$0·589\mu$	$0·760\mu$
μ . . .	2·94	3·12	2·93	2·60
k . . .	2·31	1·49	0·45	0·06
R . . .	44	35	25	20 per cent.

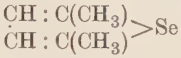
The reflecting power was also studied by L. P. Sieg; the optical constants by L. D. Weld. A. C. Schultz-Sellack said the **diathermacy** of selenium is such that a plate 3 mm. thick cuts off 13 per cent. of the heat rays emitted by lampblack at 100°; and 5 per cent. of the heat rays from a coal-gas flame. C. Cuthbertson and E. P. Metcalfe found the index of refraction of the vapour to be 1·001570 for $\lambda=546·0\mu\mu$; 1·001565 for $\lambda=589·3\mu\mu$; and 1·002370 for $\lambda=656·3\mu\mu$. W. S. Gripenberg found 3·50 for the index of refraction of crystalline selenium at $\lambda=589\mu\mu$ (orange-yellow). According to R. F. Miller, when plane polarized light is reflected from the surface of an absorbing medium it becomes in general elliptically polarized, and if the form of the elliptical vibration is determined for some angle of incidence, the optical constants of the medium may be calculated. With the crystal axis parallel to the flame of incidence, the index of refraction is 3·4 to 4·4, and when perpendicular thereto, 2·3 to 3·1. E. Schmidt found the degree of polarization, π, as a function of the angle of incidence, ψ, has a maximum at about $\psi=70°$.

ψ . . .	20°	30°	40°	60°	70°	80°	86°
π . . .	0·070	0·196	0·363	0·824	0·986	0·986	0·505

R. W. Wood found that a prism of selenium has following values for the index of refraction, μ, the absorption index, k, and the percentage reflecting power, R, for light of wave-length λ.

λ . . .	$0·400\mu$	$0·490\mu$	$0·589\mu$	$0·760\mu$
μ . . .	2·94	3·12	2·93	2·60
k . . .	2·31	1·49	0·45	0·06
R . . .	44	35	25	20

J. L. Sirks found the **dispersion** of the *A*- to the *C*-rays to be 6·5 times as great as with carbon disulphide, and $(\mu_C - \mu_A)$ 14 times as great. I. Zoppellari found the **atomic refraction** of selenium in various compounds for the H_α-, H_β-, H_γ-, and the *D*-lines. The results for the first and last of the series are summarized in Table I. The values for selenoxene are calculated on the assumption that its formula is



$$\begin{matrix} CH:C(CH_3) \\ CH:C(CH_3) \end{matrix} > Se$$

The results are taken to show that selenium in combination behaves very similarly to sulphur in respect to its refraction constants; the diversity in behaviour of selenium in its various compounds is, however, much less strongly marked than is that of sulphur. C. P. Smyth studied this subject, and J. E. Calthrop, the relation between the at. vol. and the index of refraction. K. Spangenberg studied the mol. refraction of the oxides, sulphides, selenides and tellurides. A. C. Becquerel gave 10·960 for the **magnetic rotatory power** of selenium for the *B*-line; and if $\mu=2{\cdot}6550$, $u=10{\cdot}960\mu^{-2}(\mu^2-1)^{-1}=0{\cdot}255$. M. A. Schirmann studied the polarization of light by submicroscopic particles of selenium.

TABLE I.—ATOMIC REFRACTION OF SELENIUM.

	H_α-line.		*D*-line.	
	μ-formula.	μ^2-formula.	μ-formula.	μ^2-formula.
Se (element)	30·36	11·77	—	—
$Se(C_2H_5)_2$	19·70	10·93	19·56	10·94
$Se_2(C_2H_5)_2$	21·45	11·73	21·57	11·82
Selenoxene	18·81	10·94	19·33	11·18
H_2SeO_4 41·8112 per cent. aq. soln.	15·85	8·87	16·25	9·22
,, 27·3340 ,, ,,	15·64	8·74	15·85	9·00
H_2SeO_3 22·4711 ,, ,,	15·67	8·92	15·95	9·12
,, 30·5930 ,, ,,	15·90	9·91	16·09	9·19
KSeCy 32·7722 ,, ,,	25·49	15·34	25·79	15·30
,, 43·5497 ,, ,,	25·00	14·84	25·30	15·04

As shown by C. R. Fresenius,[10] and others, selenium imparts a pale blue coloration to the flame of hydrogen; and R. Bunsen observed that selenium and its compounds impart a cornflower blue colour to Bunsen's flame. A piece of cold porcelain in the reducing flame acquires a brick-red deposit, and in the oxidizing flame a white deposit. J. Plücker in 1861 made some observations on the **spectrum** of hydrogen selenide; J. Plücker and J. W. Hittorf and others proved that selenium may show a **line spectrum** or a **band spectrum.** When the vapour of selenium, boiling in a vacuum tube, is exposed to the jar-discharge, it furnishes a line spectrum. If an ordinary discharge be passed through a vacuum tube, in which selenium is boiling, it furnishes a band spectrum. The band spectrum was obtained by G. Salet, R. Böttger, A. Mitscherlich, and G. Werther from the flame of burning selenium; and, according to E. Mulder, it can be obtained from the metalloid heated in a hydrogen flame. Sulphur under similar conditions gives a continuous spectrum, and, added E. Mulder, the spectrum of selenium becomes continuous when the vapour density is increased. The **spark spectrum** of selenium was studied by A. Ditte, R. Capron, A. S. Rao, G. Ciamician, J. Parry, E. Demarçay, G. Salet, A. de Gramont, C. Runge and F. Paschen, F. Exner and E. Haschek, R. Thalén, G. Berndt, L. and E. Bloch, A. Hagenbach and H. Konen, J. Messerschmitt, E. Goldstein, etc. The line spectrum produced by sparking from a jar discharge in a hot vacuum tube has lines at 6055 in the orange; at 5306, 5272, 5254, 5226, 5174, 5142, 5097, 5093, 4996, and 4979 in the green; and at 4845, 4841, 4761, 4648, and 4604 in the blue. The **arc spectrum** of selenium was studied by J. Stark and R. Küch, M. A. Catalan, M. Kimura, J. C. McLennan and co-workers, and J. Messerschmitt; and the **flame spectrum** by P. Böttger, G. Werther, A. Mitscherlich, E. Mulder, G. Salet, W. N. Hartley, P. Lenard, J. Messerschmitt, and J. M. Eder and E. Valenta. The bands are sharp on the violet side, shade off towards the red side of the spectrum. The bands are at 5871 in the orange-yellow; 5751 in the yellow; 5621, 5491, 5371, 5271, 5166, 5031, and 4951 in the green; and 4851 in the blue. D. Gernez observed the band spectrum of selenium is obtained as an **absorption spectrum.** At 700°, the vapour of selenium absorbs all the light with the exception of the red, but if the temp. is raised, the tint of the vapour brightens, and the different regions of the spectrum reappear furrowed with groups of black bands in the blue and violet. The absorption spectrum was studied by J. N. Lockyer, R. W. Wood, B. Rosen, J. J. Dobbie and J. J. Fox, R. Mecke, T. P. Dale, F. F. Martens, P. Lenard, and W. W. Coblentz. M. Luckiesh studied the transmission spectrum of glasses coloured yellow to deep red by selenium, Fig. 9. According to F. van Assche, a thin layer of selenium, obtained by compressing a drop of the fused substance between plates of glass at 250°, and allowing it to cool slowly under press., only transmits the rays between the spectral lines A and C. The amount of absorption increases with the thickness of the layer. When a beam of white light is passed first through a soln. of alum and then through a film of selenium, all the luminous rays are arrested. A thin film of selenium if heated to 250° is apparently opaque to all luminous radiation. A. H. Pfund determined the absorption power of crystalline selenium for light of wave-length 400$\mu\mu$ to 1000$\mu\mu$, and his results are summarized in Fig. 10, and show that the absorption increases steadily from the ultra-red to the violet. There is no marked maximum or minimum in the absorption curve near 700$\mu\mu$ where the conductivity of selenium is a maximum. G. Briegleb found that the absorption spectrum of soln. in carbon disulphide indicates that there is a change in the molecular structure of selenium in dil and conc. soln. The following values were obtained for the value of the logarithm of the mol. extinction coeff., log k, for wave-lengths, λ in $\mu\mu$:

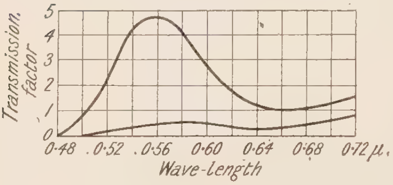


FIG. 9.—Spectral Transmission of Selenium-coloured Glass.

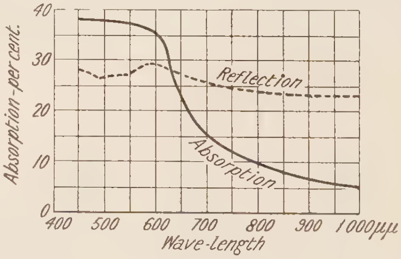


FIG. 10.—The Absorption and Reflecting Power of Selenium for Light.

Mols per litre.	Wave-lengths in $\mu\mu$.			
	422	434	447	471·3
$53·5\times10^{-4}$	2·13	2·11	1·89	1·67
$37·25\times10^{-4}$	2·22	2·11	2·01	—
$15·5\times10^{-4}$	2·27	2·16	—	—
$0·91\times10^{-4}$	2·29	2·179	2·088	1·81
$0·55\times10^{-4}$	2·45	2·346	—	2·03
$0·462\times10^{-4}$	2·45	2·4	2·30	—

A. Cornu found that the absorption in the ultra-violet increases with increasing wave-length. Observations were also made by W. Meier. W. W. Coblentz found that with a film of selenium 2 days old there is a transmission of about 20 per cent. throughout the ultra-red spectrum down to 14μ, whereas with a fresh film the transmission rose to 80 per cent. for 10μ. Like the metals, selenium is more opaque than sulphur, and unlike the non-metals it shows no selective absorption.

J. N. Lockyer and W. C. Roberts-Austen observed that in the oxyhydrogen flame, selenium furnishes a *channelled spectrum*; and J. Evershed, that a continuous emission spectrum can be obtained from heated selenium vapour. E. Paterno and A. Mazzucchelli also studied the spectrum from selenium in heated vessels. The **ultra-violet spectrum** was studied by G. Berndt, J. C. McLennan and co-workers, F. Exner and E. Haschek, P. Lacroute, and J. M. Eder and E. Valenta. The effect of *temperature* was studied by G. Ciamician; the effect of *pressure*, by G. Ciamician; the effect of a *magnetic field*, by J. Plücker, G. Berndt, and J. Chautard; the *self induction*, by A. de Gramont; and the *enhanced lines*, by F. E. Baxandall. The *spectrum of the cathode luminescence* was studied by P. Lewis; the **resonance spectrum**, by B. Rosen, who gave $\gamma = a - 397 \cdot 5n + 1 \cdot 32n^2$, where a is 27423 for the exciting mercury line 4046. B. Schmidt also observed the series $\lambda^{-1} = 22312 - 362m + 1 \cdot 3m^2$ in the resonance spectrum. W. Steubing found that a magnetic field had no effect on the resonance and fluorescence spectra. V. Ehrenfeucht also studied the subject.

The compound line spectrum of selenium generally resembles the corresponding spectrum of sulphur. A. Fowler said that in the diffuse series of triplets, many of the brighter components are accompanied by fainter lines or satellites. The first line of a triplet appears to have a satellite on the more refrangible side, while the second has a satellite on the less refrangible side; and the third line in three of the triplets has a satellite nearly the same brightness as itself. The regularities in the **series spectrum** of sulphur have been discussed by A. Fowler, W. M. Hicks, J. C. McLennan and co-workers, G. Ciamician, R. A. Sawyer and C. J. Humphreys, C. Runge and F. Paschen, H. N. Russell, B. Dunz, D. K. Bhattacharjya, P. Pattabhiramayya and A. S. Rao, T. L. de Bruin, and M. A. Catalan.

The high frequency spectrum, or the **X-ray spectrum,** in the K-series has been studied by W. Duane and K. F. Hu,[11] B. Walter, L. H. Martin, J. Schrör, A. Leide, G. L. Pearson, W. Bothe and H. Fränz, R. Edlen, B. C. Muherjee and B. B. Ray, S. Björck, and M. Siegbahn and E. Fremann, and they gave for $\alpha_2\alpha'$, 1·109; for α, α, 1·104; and for β, β, 0·993. For the L-series, E. Hjalmar, A. Leide, D. Coster, R. Thoroeus, J. Schrör, W. Bothe and H. Fränz, W. Bothe, B. C. Muherjee and B. B. Ray, S. Björck, G. L. Pearson, and D. Coster and F. P. Mulder gave α, α, 8·9706; $\alpha_3\alpha''$, 8·9386; and for β, β, 8·7172, etc.; S. Björck, D. Coster and F. P. Mulder, studied the M-series; and S. Björck, the N-series. C. T. Chu studied the soft X-rays from selenium; H. W. Edwards, the reflection of X-rays.

N. Piltschikoff[12] studied the Moser rays emitted by selenium. F. Diestelmeier, and W. Steubing found that oxygen and the vapours of sulphur, selenium, and tellurium exhibit **fluorescence,** and that the fluorescence moves from regions of short wave-length to regions of longer wave-length with increase of atomic weight. For oxygen, fluorescence is exhibited below λ2000 A.; for sulphur, between λ2500 A. and λ3200 A.; for selenium, from λ3000 A. into the visible region, and for tellurium in the most refrangible part of the visible region. The fluorescence spectra are discontinuous, and show more or less feeble groups of lines which have the appearance of bands. The fluorescence is greatly weakened by mixing the vapours with other gases or vapours. The fluorescence is only observable when the vapours are of low density compared with that of the sat. vapours, and the influence of temp. on the intensity of the effect would seem to show that centres of emission are the diatomic molecules. The phenomenon is very sensitive to foreign substances, and no fluorescence is observed in the presence of small quantities of impurities. The fluorescence spectra consist of bands which are shaded off towards the red end of the spectrum. As the atomic weight increases, the " centre of gravity " of the exciting light shifts from the ultra-violet into the visible region. In each case, changes are found to occur in the fluorescence spectrum when the nature of the exciting light is changed. H. Konen discussed this subject. R. Robl observed no fluorescence occurs with selenium in ultra-violet light. J. C. McLennan and co-workers, the fluorescence of selenium vapour. B. Rosen studied the **fluorescence spectrum ;** and W. Kessel, the resonance spectrum.

F. Ehrenheft showed that while sulphur particles move in a direction opposite to that of the beam of light—negative photophoresis—selenium particles, under some conditions, dependent on the duration of heating in the preparation of the selenium, have a positive **photophoresis** for they move in the direction of the beam of light; but I. Parankiweicz showed that with particles of selenium 8×10^{-6} to 60×10^{-6} cm. in diameter, the negative photophoresis is nearly 6 times as great as the force of the same light beam on sulphur particles of the same mobility. The negative photophoresis is a maximum with particles of radius 15×10^{-6} cm. The negative photophoresis is independent of time, but the positive photophoresis is a function of time and is independent of the surrounding gas and of the press. The power of reaction of positive selenium on light decreases with time. The independence of the photophoric force on the press., the chemical nature of the surrounding gas, the decrease of the positive reaction of selenium particles which is due to an internal change of the selenium, and, further, the fact that particles of different materials, but of the same mobility, are very differently acted on by light, all tend to confirm the conclusion of F. Ehrenhaft that the action is a direct one of the light on the material. M. Hake, and J. Mattauch studied this subject. The mass absorption coefficient, λ/D, for the X-rays when I_0 is the intensity of the beam of homogeneous radiation, the intensity I at a depth x is $I=I_0e^{-\lambda x}$, and D is the density given by C. G. Barkla and C. A. Sadler [13] for a selenium radiator, is

	C	Mo	Al	Fe	Ni	Cu	Zn	Ag	Sn	Pt	Au
λ/D .	2·0	16	19	116	141	150	175	88	112	93	100

The coeff. of absorption μ for β-rays was found by J. A. Crowther to be for selenium, $\mu/D=8\cdot65$. H. Müller observed that exposing selenium to intense α-rays had no effect on the induced radioactivity; and W. G. Guy could detect no evidence of **radioactivity.** J. E. Wagstaff gave $4\cdot06\times10^{12}$ for the **vibration frequency ;** W. Herz gave $2\cdot74\times10^{12}$. A. D. Udden found the **ionization potential** of the vapour to be 12·7 volts; G. Piccardi gave 9·02 volts. E. Rupp studied the absorption of electrons by selenium.

P. A. von Bonsdorff [14] found that selenium becomes electrified when it is rubbed in dry air; and P. E. Shaw and C. S. Jex said that the **triboelectricity** is negative when selenium is rubbed with glass. J. J. Berzelius, and P. Riess said that the **electrical conductivity** of selenium—probably the vitreous form—is so small that it is a non-conductor of electricity; and G. J. Knox found that molten selenium is a conductor. J. W. Hittorf showed that the vitreous form of selenium is a good insulator, while the metallic form is a conductor; the conductivity increases with a rise of temp. until the m.p. is reached, when the resistance then suddenly increases. P. von Schrott found that red crystalline selenium, like the red amorphous powder, is a non-conductor of electricity. K. F. Herzfeld, and A. Günther-Schulze discussed the metallic conductivity of selenium. The sp. **electrical resistance** of grey metallic selenium varies with the history of the preparation—temp., direction of heating, rate of cooling, the purity and dryness of the materials—as well as on the nature of the electrodes. Hence, there are some discrepancies in the published data. E. W. von Siemens gave for the sp. resistance, 376,000 ohms; F. Weidert, 239,000 ohms; and P. von Schrott, 252,000 ohms for a sample obtained by heating vitreous selenium 5 hrs. at 195°, and 2 hrs. at 210°–215°, while if crystallized by long standing in quinoline, powdered and pressed into cylinders the resistance was $6\cdot8\times10^{8}$ ohms. If powdered selenium be compressed into cylinders, the resistance is always greater than when massive selenium is used. C. Ries said that ordinary selenium used in making cells has a resistance of 10,000 to 100,000 ohms, and that 50,000 ohms may be taken as the best representative value. S. Datta represented the resistance, R, at different temp., θ, by $R\times10^{-5}=63{\cdot}01-0{\cdot}86-0{\cdot}0029\theta^2$. H. Pélabon gave $\log R=8{\cdot}506-0{\cdot}0095\theta$ ohms between 390° and 600°; at 300°, the resistance decreases suddenly to a minimum, it then rises to a maximum and then diminishes. Thereafter, the resistance depends on the treatment. He attributed the enormous variations in the resistivity of grey selenium with heat treatment to the presence of variable proportions of a variety α-selenium which is very resistive, and β-selenium which is very conductive. The sp. resistance of selenium cooled slowly from the molten state is several millions of ohms. at 15°, and it contains a high proportion of α-selenium. If the selenium, heated to near its b.p., is allowed to cool, it contains β-selenium, and its resistance is only a few ohms. Warming α-selenium causes a rapid decrease in resistance until at 200° it is 7×10^4 ohms.; fusion at 218° is attended by a sharp increase in the resistance.

R. Marc's *A*- or metallic selenium is a non-conductor and the *B*-form is a conductor. If amorphous selenium be heated from room temp. to about 60°, there is no sign of electrical conductivity; at about 60° the selenium acquires a small conductivity, and this increases with rise of temp. but it is still small at 90°. If the specimen be now cooled to ordinary temp. it is as before a non-conductor. If heated above 90°, the selenium becomes grey, and its conductivity is greater than before, and it remains a conductor when cooled to ordinary temp. If the temp. is raised to 125°, the conductivity is much greater and it increases rapidly to a maximum at the m.p., 217°. Between 217° and 250°, the conductivity rises slowly with rise of temp. Selenium which has not been heated above 100°–170° has a marked electrical resistance at ordinary temp., and, like carbon, the temp. coeff. of the resistance is negative for the resistance decreases with rise of temp. The small conductivity of the *A*-form of metallic selenium was attributed by R. Marc to the presence of a trace of selenium dioxide. M. Coste, P. von Schrott, R. Marc, A. Pochettino and G. C. Trabacchi, etc., also studied this subject.

When selenium is heated up to 180°–200° it shows a rapid increase of conductivity with *temperature*; and if the temp. be kept constant for a long time, the conductivity rises slowly to a maximum. The higher the constant temp., the more rapidly is this maximum attained; thus, it requires 12–24 hrs. at 210°, and 3 days at 180°. If selenium which has attained its maximum conductivity at a temp. exceeding 200° be rapidly cooled to the temp. of the room, the conductivity increases in a way which is characteristic of the metals; this augmented conductivity, however, is not retained permanently, but it falls at first rapidly and then slowly to a minimum value. The time required for this change depends on the process of heating, and on the purity of the preparation. Selenium when heated to 200°–215° so as to attain its maximum conductivity, and then rapidly cooled, has a positive temp. coeff. like the metals; if cooled not so rapidly, there is only a moderate increase in the conductivity; and if cooled slowly the conductivity shows first a maximum and then a minimum. The position of the maximum varies with the velocity of cooling. So also if the specimen has not attained its maximum conductivity, and is rapidly cooled, its conductivity varies with its history, and the conductivity-temp. curve shows a maximum and a minimum at different temp. Thus P. von Schrott obtained the results illustrated by the curves in Fig. 11. Curve 1 represents a sample heated for 5 hrs. at 210°–215°, and slowly cooled. The maximum occurs at 185°, and the minimum at 120°—the temp. coeff. between 135° and 120° is positive and negative elsewhere. Curve 2 represents a specimen heated to 210°, and it has a maximum at 140°, a minimum at 100°, and a positive temp. coeff. between 140° and 100°, and negative elsewhere. The sample represented by curve 3 was heated a short time at 200°–215°, and it behaves like a metal between the maximum at 50° and the minimum

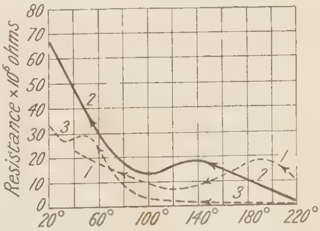


FIG. 11.—The Electrical Resistance of Metallic Selenium.

at 30°—*vide* also Fig. 11. If selenium be heated to 210° the maximum on the cooling curve is in a different position to the maximum on the heating curve. P. von Schrott obtained the results indicated in Fig. 12. The maximum on the heating curve is at 130°, and on the cooling curve at 90°. L. S. McDowell found that the increase in resistance of selenium with decrease of temp. continues down to the temp. of liquid air, when the cell becomes almost entirely non-conducting. The effects of *pressure*, and of the voltage of the impressed *electromotive force* are indicated below.

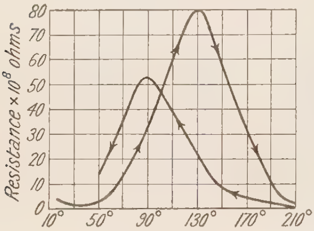


Fig. 12.—Electrical Resistance on a Rising and a Falling Temperature.

The presence of *impurities*—moisture, and metals—has a great influence on the temp. coeff. of selenium. If dried amorphous selenium be warmed slowly to the m.p., the conductivity increases regularly as the temp. rises above 90°; but with moist selenium there occur decreases in the conductivity with a rise of temp. between 110° and 130°, and 200° and 217°. The phenomena are connected with the loss of moisture. Moist selenium, as shown by E. W. von Siemens, R. Marc, P. von Schrott, and C. Ries, has a greater conductivity of moist selenium. The conductivity of moist selenium decreases with the passage of a current at first rapidly, then slowly. Moist selenium attains its maximum conductivity with cooling more easily than dry selenium. R. Marc showed that the presence of the noble metals—especially silver—accelerates the transformation of selenium into the metallic form. The maximum appears more quickly and sharper the higher the proportion of silver between 0·03 and 1·4 per cent. Platinum also gave good results; copper not as good; and iron did not act at all. S. Bidwell was so impressed with the favourable effect of small additions of metal impurities on the conductivity of selenium that he attributed the peculiar action of light on that element to the presence of selenides. R. Marc, W. von Uljanin, M. Sperling, and L. Amaduzzi and M. Padoa, however, found that in some cases, the sensitiveness of selenium to light is decreased by impurities; and L. Amaduzzi and M. Padoa found that amorphous mixtures of sulphur and 88·99 and 95·884 per cent. of selenium have photoelectric sensibilities expressed as the ratio of the conductivities in light and in darkness respectively as 1·20 and 3·6. The second mixture is freely sensitive to variations of strong light, the first is scarcely sensitive at all. The hysteresis is different in the two mixtures. Isomorphous mixtures of sulphur with from 0·887 to 10·081 at. per cent. of tellurium gave a sensitiveness curve which fell rapidly at first and then slowly as the proportion of tellurium increases.

E. W. von Siemens examined the effect of *time* on the conductivity. He said that selenium prepared by heating the amorphous element to 100° for many hrs. conducts electricity electrolytically, *i.e.* it is a better conductor at a high than at a low temp.; but if heated for, say, 10 hrs. at 200°–210° it then conducts like a metal in that the conductivity decreases when heated and increases when cooled. E. Weidert observed that 0·5 to 2 hrs. heating suffices to show this effect. The second of these varieties is also obtained by slowly cooling molten selenium. E. W. von Siemens assumed what he regarded as a third variety of crystalline selenium to be stable at 200° and transformed into the first variety at lower temp. The third variety was considered to be a better conductor than the other forms, and to be more sensitive to light. E. W. von Siemens assumed that the maximum and minimum points obtained with cooling selenium, *e.g.* Fig. 11, are due to a gradual transformation of the second to the first variety, and that by rapid cooling below 0°, the transformation of metallic selenium is complete. This, however, does not agree with P. von Schrott's or with C. Ries's observations. The transition points were found by C. Ries to assume an approximately constant value after some days, and to be independent of comparatively wide fluctuations of temp. under 90°. Thus, a preparation with a maximum resistance at 23° retained the same value after 15 years although the specimen was frequently employed in experimental work. The conductivity curve of this sample is illustrated by Fig. 13, and it shows two maxima and two minima. C. Ries found that a specimen of selenium heated over 200°, and then rapidly cooled, suffered a marked change in its reaction during the first ten days—*vide* Fig. 14, but even after 20 days it had not attained a constant value although subsequent changes were small. J. Luterbacher also observed that the selenium may take three weeks before its resistance attains an approximately constant value, although months afterwards irregularities may appear. R. Marc observed that the presence of the noble metals shortens the time required for the element to assume equilibrium and attain a constant state—*e.g.* in the presence of 0·01 to 0·4 per cent. of silver, the resistance of selenium assumes the constant state in a few hrs. M. Coste found that immediately after the conversion of vitreous to metallic selenium, the resistance of a rod 90×1×0·5 mm. was 44,000 ohms; 60,000 ohms after one hr., 63,500 ohms after two hrs., 78,000 after twenty-four hrs.; and constant at 86,000 ohms. after forty-eight hrs. E. Berger found that when selenium is quenched from different temp., the resistance with and without the addition of silver reaches a minimum when the selenium is quenched from about 215°—Fig. 15. This is taken to mean that the minimum represents the formation of a compound of allotropes A and B to form Se_{AB}, and that when quenched below this temp., the A-form predominates, and above this temp., the B-form. The results were:

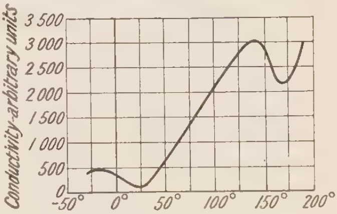


Fig. 13.—Temperature-Conductivity Curve.

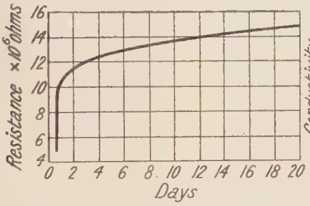


Fig. 14.—Effect of Time on the Resistance of Selenium.

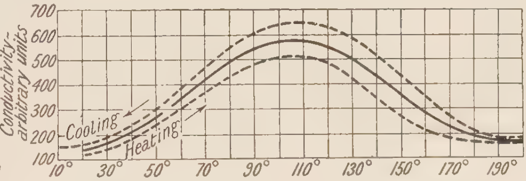


Fig. 15.—The Electrical Conductivity of Selenium on Heating and Cooling Curves.

Quenching temp.	195°	204°	209°	214°	217°	219°
R ohms—Se alone	2130	1870	1800	1790	1820	2780
R ohms—Se and silver. .	2620	2300	2030	—	2540	3040

R. Marc heated a specimen of selenium from 26° to 201° in jumps of 30° and kept the element at each temp. until the resistance was approximately constant; similarly on cooling from 201° to 19°. The results are represented by the dotted lines in Fig. 15. In each case, there is a maximum in the curve at about 100°; and both curves have the same general form, but the conductivities on the heating curve are less than on the cooling curve. On the heating curve the results are low if equilibrium has not been attained and conversely on the cooling curve. The differences in the values on the heating and cooling curves represent hysteresis phenomena; and if a longer time were allowed, so that equilibrium can be attained, it is supposed that both curves would coalesce into the continuous curve of Fig. 15. Hence R. Marc assumed that selenium exists in two forms, which exist together in solid soln., and that there is a state of equilibrium between the two forms so that at each change temp. equilibrium is displaced in favour of another state, and that time is needed for the two forms to assume that state characteristic of the given temp.—*vide supra*. These results explain the discrepancies between the measurements of different observers for the electrical conductivity of selenium, this depends on the mode of preparation, and previous history of the element—temp. at which it has been heated, the duration of the heating, the speed of cooling, and that degree of purity of the selenium.

S. Bidwell said that when the temp. is a few degrees higher than the average temp. of air, a maximum resistance is obtained, and if the heating be continued, the resistance begins to decrease. This was not confirmed by S. Datta, who found that with cast selenium annealed at 200° and subsequently at 170° until the maximum conductivity was attained, and protected from light, the resistance is intimately connected with the time taken in producing the variation in temp. Not only does it depend on the rate of heating or cooling, as the case may be, but the future behaviour of the selenium depends very much upon the period during which it is kept at a fixed temp. before being subjected to a variation in temp. If selenium after being annealed is brought down to room temp. and maintained at that temp. for a considerable time, and then subjected to a change in temp., the change in resistance is much less than when the selenium is immediately before brought down from a somewhat higher temp., or, in other words, the shape of the resistance temp. curve is less steep when the temp. is changed after a long period of constant temp. And this occurs not at room temp. alone, but at all temp. up to about 120°. It seems as if, after long being maintained at a constant temp., the selenium is sluggish in changing its physical properties connected with a variation in temp. The following determinations of the resistance, $R \times 10^5$ ohms, were made by changing the temp. of the selenium so slowly as to eliminate discontinuities due to resistance lag :

	0°	65°	20°	40°	60°	78°	100°	120°	160°	170°
R .	66·0	59·1	49·1	34·6	23·8	15·4	8·0	3·5	1·7	2·0

The results can be represented by the curve $R=(65{\cdot}01+0{\cdot}86\theta+0{\cdot}0029\theta^2)10^5$, for θ between 0° and 170°. There is no sign of any increased resistance below 170° ; and above this temp. the element begins to sublime. This prevented measurements being made at a higher temp. although the results all show an increase in the resistance. The constants of the equation depend on the annealing and past history of the element. A change of colour accompanies the change in resistance on warming crystals of selenium produced by sublimation. If a transformation into allotropic forms occurs, as seems probable, this takes place at all temp. and the various modifications are in dynamic equilibrium, the quantity of each variety depending on the temp. The degree of stability of each modification depends on the time during which it is maintained at one temp. H. Pélabon found that the electrical conductivity of liquid selenium rises rapidly with temp. up to the b.p., 690°. On cooling it again, the conductivity decreases with the same velocity. The slow cooling of selenium first melted and then heated at 690° results in the production at the ordinary temp. of a grey selenium, the conductivity of which is not constant for a given temp., but can be diminished at will by slight heating and cooling. This form of selenium does not undergo reversible transformations, its properties varying with the states through which it passes—*vide supra,* allotropes of selenium. K. J. Dieterich found the sp. resistance of crystals of selenium decrease with increasing temp. with a slight increase between 0° and 50°. R. de Laer Kronig studied the effect of electronic bombardment on the conductivity.

In 1873, W. Smith discovered what has proved to be a most remarkable property of selenium ; it is sensitive to *the action of light.* He said :

> Being desirous of obtaining a more suitable high resistance for use at the Shore Station in connection with my system of testing and signalling during the submersion of long submarine cables, I was induced to experiment with bars of selenium, a known metal of very high resistance. I obtained several bars varying in length from 5 to 10 centimetres, and of a diameter of 1 to 1½ millimetres. Each bar was hermetically sealed in a glass tube, and a platinum wire projected from each end for the purpose of connection. The early experiments did not place the selenium in a very favourable light, for the purpose required, for although the resistance was all that could be desired—some of the bars giving

1,400 megohms absolute—yet there was a great discrepancy in the tests, and seldom did different operators obtain the same result. While investigating the cause of such great differences in the resistance of the bars, it was found that the resistance altered materially according to the intensity of light to which it was subjected. When the bars were fixed in a box with a sliding cover, so as to exclude all light, their resistance was at its highest, and remained very constant, fulfilling all the conditions necessary to my requirements, but immediately the cover of the box was removed, the conductivity increased from 15 to 100 per cent. according to the intensity of the light falling on the bar. Merely intercepting the light by passing the hand before an ordinary gas burner placed several feet from the bar increased the resistance from 15 to 20 per cent. If the light be intercepted by rocksalt or by glass of various colours, the resistance varies according to the amount of light passing through the glass. To ensure that temp. was in no way affecting the experiments, one of the bars was placed in a trough of water so that there was about an inch of water for the light to pass through, but the results were the same; and when a strong light from the ignition of a narrow band of magnesium was held about nine inches above the water the resistance immediately fell more than two-thirds, returning to its normal condition immediately the light was extinguished.

The lowering of the electrical resistance of selenium by exposure to light was confirmed by M. Sale, the Earl of Rosse, W. G. Adams, etc. The effect is produced by lamp or candle light filtered through a plate of sodium chloride or coloured glass to cut off the heat rays. S. Datta, indeed, showed that not more that 0·04 of the effect produced by light can be attributed to the heat produced by light. B. Gudden and R. Pohl attributed the photoconductivity primarily to the liberation of electrons inside the crystals by absorbed light, while secondary effects are produced by the positive charges left behind in the crystals. Two kinds of crystals were observed: (i) those in which the primary ionization takes place in the pure crystal material – selenium, cinnabar, zinc blende, diamond, sulphur, etc., and (ii) those in which the ionization is located in impurities of irregularities in the crystal structure – *e.g.* coloured quartz, and alkali iodides. The crystals of the first class have all a refractive index greater than 2, and all crystals with the index greater than 2 exhibited photoconductivity.

The *unit of illumination* is the *lux*—plural *luces*—which is the intensity of light at a distance of one metre from a standard candle; and the so-called *foot-candle* which is the intensity of light at a distance of one foot from a standard candle. The relation between these two units is represented by the formula: luces = 10·75 foot-candles. The illumination values are calculated from: luces = candle power divided by the square of the distance in metres; or foot-candles = candle power divided by the square of the distance in feet.

In the ordinary **selenium cell,** the variation of the electric resistance of the element when exposed to light is measured on a suitable galvanometer. The term "cell," therefore, is not used in the same sense as is usually understood, and G. W. White preferred the term *selenium bridge*, and L. B. Crum, *selenium unit*. In the construction of selenium cells, the resistance of the selenium is so high that it is advisable to arrange the selenium so that only a short length need be traversed by the current; and that a large sectional area of selenium be used in order that as much current as possible may pass through the selenium; further, since only the exposed portion of the selenium suffers a change of resistance with illumination, a comparatively large surface with respect to its vol. should be exposed to the light—this means that thin layers of selenium must be used. The preparation of thin films of selenium was described by M. Reinganum, A. H. Pfund, W. S. Gripenberg, and G. von Salviati. In 1876, E. W. von Siemens constructed the first selenium cell; it consisted of two platinum wires wound in a flat double spiral, and attached to a sheet of mica; the sheet and wires were then coated with molten selenium, exposed to a temp. of 200° for some hours, and slowly cooled. This process of long heating and slow cooling is called *annealing*. Selenium of a high degree of purity is employed, but when alloyed with 0·01 to 0·1 per cent. of silver R. Marc showed that the recovery of the cell may be hastened as indicated above. V. Chiarini said that red selenium is more sensitive to changes of light than is the case with black selenium. E. Ruhmer prepared what he called *soft cells* in which the selenium is coarse-grained, and obtained by annealing at 200° followed by slow cooling; and *hard cells* in which the selenium is fine-grained, and obtained by annealing at a somewhat lower temp. followed by rapid cooling. Hard cells have a greater resistance than soft ones, and suffer a relatively smaller change in resistance with illumination. The soft cells are very sensitive to feeble illumination, but their resistance with strong illumination is smaller than with hard cells. This is illustrated below. A longer time is required by a hard cell than by a soft cell to assume its equilibrium resistance value on exposure to light; and the recovery of its resistance on cutting off the light is faster with hard cells than with soft cells. The *sensitiveness* of a selenium cell is the ratio of its resistance in the dark to its resistance when exposed to the given source of illumination. The illumination produced by bright sunlight at noon on a winter's day approximates 20,000 luces, so that the sensibilities of the soft and hard cells indicated below are respectively $120,000/1500=80$, and $100,000/6000=16·6$. E. Ruhmer has constructed cells with a sensibility exceeding 200. Numerous different forms of selenium cell have since been devised with the idea of decreasing the resistance and increasing the exposed area of the selenium as much as possible.

Most selenium cells can be divided into two groups according as the light falls vertically or parallel to the direction of the electric current in the selenium. The relative merits of the two forms were discussed by M. Sperling, G. W. White, A. M. Tyndall and G. W. White, C. Ries, and W. S. Gripenberg. Cells of the first type, made from wire or ribbon, were described by S. Bidwell, E. W. von Siemens, E. Mercadier, A. G. Bell, A. F. Weinhold, O. von Bronk and E. Ruhmer, V. K. Zworykin, R. Marc, E. Ruhmer, R. Hart, etc. Cells of the first type made by ruling or engraving lines across a thin layer of, say, silver, or, say, glass on carbon, and filling up the gap with selenium were made by G. von Salviati, R. E. Liesegang, B. Glatzel, E. E. Fournier d'Albe, C. Ries, E. Presser, W. S. Gripenberg, O. Linder and B. J. Replogle, A. Righi, A. C. Longden, J. W. Giltay, etc. Cells of the second type were made by A. M. Tyndall and G. W. White, W. S. Gripenberg, G. Dragonetti, C. E. Fritts, A. Righi, W. von Uljanin, H. Küchenmeister, J. Neale, R. E. Martin, H. Thirring, J. L. Baird, R. Hart, etc. A. O. Rankine, and T. Baker found that some cells with direct current show appreciable and persistent polarization effects which disappear when the cells are operated by alternating currents and the cells then show an enhanced light sensitivity. A. Mickwitz used the selenium cell as a colorimeter.

The increase in the electrical conductivity which occurs where selenium is exposed to light is such that with cells of low resistance the conductivity increases rapidly at first, and then more and more slowly—*A*, Fig. 16; while with cells of high resistance or high sensitiveness, the conductivity rises to a maximum value and then falls off more and more slowly—*B*, Fig. 16. In both cases there is an increase in conductivity immediately after exposure to light. C. Ries mentioned a case where the conductivity of the cell fell off so much that on the fifth day it had reached a lower value than that shown in darkness. He attributed this anomalous result to the presence of moisture. F. C. Brown, however, prepared cells which had a low resistance, and a sensitiveness never above 20 per cent., and which decreased their conductivity immediately after exposure to light—*C*, Fig. 16. These cells were said to be *light-negative cells* in contrast with the *light-positive cells* whose conductivity always increased when exposed to light. O. Weigel inferred that the light-sensitiveness of selenium is due to the contained water reducing the resistance, although this does not agree with his observation that the light-sensitiveness in vacuo is greater than it is in free air, and with C. Ries's observation that the light-sensitiveness of dry preparations of selenium is decreased by moisture. This is in harmony with the experiment of P. von Schrott, and A. Pochettino and G. C. Trabacchi. Observations on this subject were also made by F. C. Brown, and L. B. Crum. C. Ries concluded that the so-called light-negative property of selenium is not a specific property of the element, but is a secondary effect

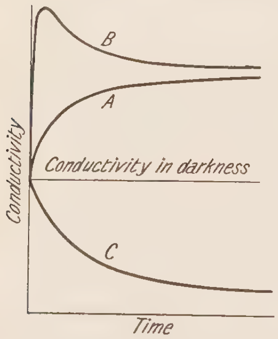


FIG. 16.—Types of Change of Electrical Conductivity on Exposure to Light.

produced by moisture or other impurities. W. Flechsig studied the effect with crystals of selenium.

The effect of light of different *intensity* on the resistance of selenium expressed in R ohms, with an applied e.m.f. of 10 volts, with light of intensity, I luces, is illustrated by the following observations by E. Hausmann with E. Ruhmer's soft cylindrical and hard flat cells respectively:

Soft I	0	1	2	4	16	64	256	1,600	20,400
Cell R	120,000	42,000	32,000	25,000	15,000	9,000	5,000	3,050	1,500
Hard I	0	4,09	8,00	22,2	200	555·6	800	5,000	20,000
Cell R	100,000	75,000	66,000	54,000	35,000	26,000	23,000	14,000	6,000

Observations were made by C. Ries, V. P. Barton, A. Korn and B. Glatzel, C. Carpini, M. Sperling, W. Jänichen, R. J. Piersol, etc. C. Carpini found that the curve varies according as the light intensity is being raised or lowered. V. P. Barton measured the change of electrical resistance produced by light between 4300 A. and 9300 A., and observed a maximum decrease at 7000 A. The Earl of Rosse, W. G. Adams, and G. Berndt assumed that the resistance, R ohms, is universally proportional to the square root of the light intensity, I luces, so that $R=aI^{-\frac{1}{2}}$, where a is a constant. This equation does not give good results even as a rough approximation for intense illuminations, but it is valid for light of moderate intensity. A. H. Pfund found this relation applies for the spectrum from the violet to the yellow, and P. J. Nicholson found that it holds from $230\mu\mu$ to $900\mu\mu$. E. W. von Siemens, and E. A. Hopius assumed that the resistance is inversely proportional to the cubic root of the intensity of light so that $R=aI^{-\frac{1}{3}}$, where a is a constant. The results with this equation are moderately accurate, and give rough approximations, but for more intense illumination the index has to be changed again. A. H. Pfund, and E. Ruhmer found that the resistance can be represented by $R=aI^{-\beta}$, where a and β are constants which can be valuated from two observations R_1 and R_2 with corresponding values of I_1 and I_2, when $\log R_1-\log R_2=\beta(\log I_2-\log I_1)$. For the selenium employed by A. H. Pfund, the so-called *illumination constant* $\beta=0·510$ for light of wave-length $\lambda=450\mu\mu$; $0·712$ for $\lambda=696\mu\mu$; and $\beta=1$ for $\lambda=711\mu\mu$ to $830\mu\mu$. E. Ruhmer found that β ranged from 0·25 to 0·42. N. A. Hesehus gave the relation $I=a(b^m-1)$, where a and b are constants, and m denotes the relative change in the resistance such that $R_{\text{light}}=R_{\text{dark}}(m+1)^{-1}$. For the selenium employed by N. A. Hesehus, $a=5$, and $b=2$. E. Presser gave $R=a(I+b)^x$, where a and b are constant, and x is a measure of the softness of the cell, and lies between 1·0 and 1·5 being nearer unity the harder the cell. G. Athanasiadis gave $I=K(K-a)b$, where a and b are constants and K represents the conductivity of selenium, $R^{-1}10^5$, so that $R=a+(a^2+4Ih^{-1})^{-\frac{1}{2}}2\times10^5$. M. Sperling gave $K=a\log(1+bI)$, where a and b are constants depending on the wave-length of the light. G. M. Minchin gave an expression which reduces to $\log(R_0/R)=(I/I_1)^n\log(R_0/R_1)$, where I_1 is the intensity of the light which alters the initial resistance R_0 of the cell in darkness to R_1; I is the intensity of the light which alters R_0 to R; and n is a constant—R_0 is known, the ratio R_0/R_1 can be measured for an illumination of intensity, I_1, and the resistance R can then be calculated for an illumination I. The expressions of N. A. Hesehus, E. Ruhmer, G. Athanasiadis, M. Sperling, and G. M. Minchin give very fair results. P. von Schrott, M. Sperling, C. Ries, and F. C. Brown and J. Stebbins have shown that the sensitiveness to light of a cell made from well-crystallized selenium with a negative temp. coeff. of the resistance decreases when heated from room *temperature* up towards the m.p. The decrease is at first rapid and then slows down until in the neighbourhood of 200° it almost vanishes. A. Pochettino observed that the sensitiveness to light is very great at temp. below 0°, and he found a maximum effect at −40°, and at the temp. of liquid air the sensitiveness is about a quarter of its value at room temp. C. Ries doubted if the maximum at −40° is really an effect of the light; he believed that the sensitiveness to light, E per cent.—where $E=100(R_{\text{dark}}-R_{\text{light}})/R_{\text{dark}}$—changes with the temp. in the same way as the electric resistance, and a maximum in the resistance curve corresponds with a maximum in the sensitiveness to light. This is proved by the observations of R. Marc, illustrated by Fig. 17. L. S. McDowell found that the action of heat and light in producing a change in the conductivity of selenium is identical. The change in conductivity due to excitation by light of the same intensity takes place more slowly at low temp. than at ordinary temp., but the final change produced by sat. is enormously greater. B. Glatzel found that the sensitiveness and resistance increased continuously as the temp. fell from 0° to −70°. P. von Schrott observed irregularities when incompletely crystallized selenium was employed; and he obtained the results summarized in Fig. 20 by the use of white, red, and green light. E. O. Dieterich measured the effect of *temperature* on cells in which no maximum occurs in the red, and found that the sensibility in the blue end decreases markedly with rise of temp., while it is scarcely affected in the red end—Fig. 20. The resistance at 33° is 223,500 ohms; at 61°, 334,000 ohms; at 81·5°, 181,000 ohms; and at 132°, 195,000 ohms. In another type of cell with a maximum in the red, the maximum is displaced towards the red with rise of temp.—Fig. 20. D. S. Elliot found that at the temp. of liquid air, the maximum shifted towards the shorter wave-length.

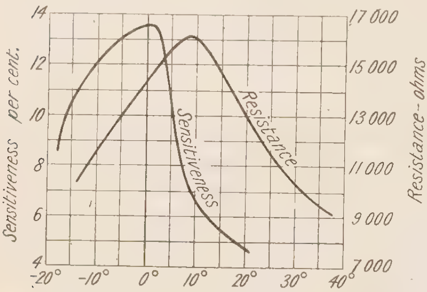
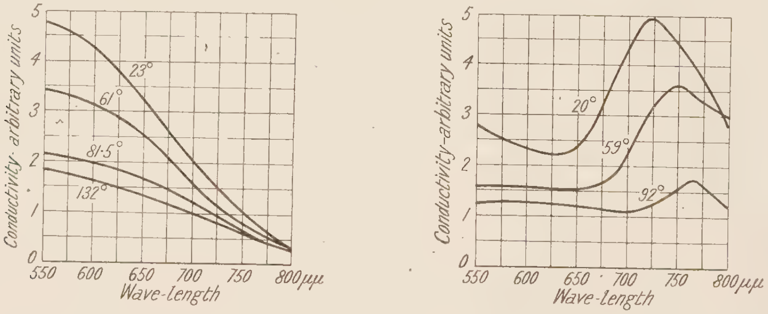


FIG. 17.—The Effect of Temperature on the Electrical Resistance and Sensitiveness to Light of Selenium.



FIGS. 18 and 19.—The Effect of Temperature on the Electrical Conductivities of Selenium Exposed to Light of Different Wave-lengths.

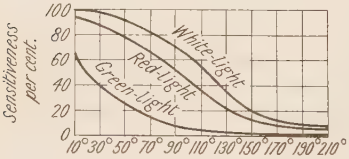


FIG. 20.—The Effect of Temperature on the Sensitiveness of Selenium to White, Red, and Green Light.

Light of different *wave-length*, or *colour* affects differently the resistance of selenium. A. H. Pfund's observations of the resistance—expressed in terms of the deflections of the galvanometer—are plotted in Fig. 21. The results show that while the blue and infra-red regions have but little effect, light of wave-length 700μμ produces a considerable change in the resistance. P. J. Nicholson extended these observations with the ultra-violet and found, as did A. H. Pfund, a maximum for 700μμ, Fig. 21; a minimum in the vicinity of 600μμ, and a maximum at about 500μμ. Observations have also been made by M. Sale, W. G. Adams, E. W. von Siemens, G. Berndt, L. A. Forsmann, B. Gudden and R. Pohl, V. P. Barton, M. Sperling, F. C. Brown and co-workers, M. Abonnenc, A. Cornu, E. O. Dietrich, A. Pochettino, P. J. Nicholson, R. Marc, and D. S. Elliot. A. Mickwitz studied the use of the selenium cell as a colorimeter. According to F. C. Brown, the sensitiveness of selenium to light rays of different colour depends on the mode of crystallization of the selenium, on the intensity of the light, on the duration of the exposure, on the previous illumination and the temp. In general, the selenium contains many kinds of crystals of different sensitiveness. Grey crystalline selenium has no characteristic curve for colour sensitiveness; and in a selenium cell there are probably many kinds of crystals with different sensibilities. In nearly all available spectra red light possesses more energy than the other colours; and while red light is most effective in lowering the resistance of selenium, that element is perhaps most sensitive to blue light, meaning that blue light is more effective in its action than is red light possessing the same energy. The law of the light action is the same for all kinds of light though the amount of action differs from colour to colour. Selenium, however, is not markedly selective towards any particular colour provided all possess the same energy. Red light from terrestrial sources has more energy than other colours, but as the source of illumination gets hotter, the maximum of energy shifts from the red end of the spectrum towards the violet.

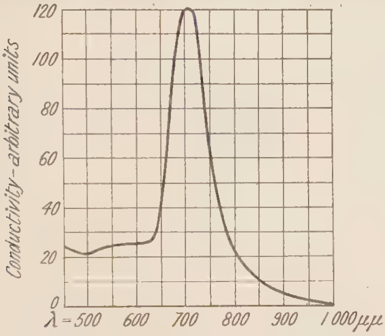


Fig. 21.—The Effect of Light of Different Wave-length on the Electrical Conductivity of Selenium.

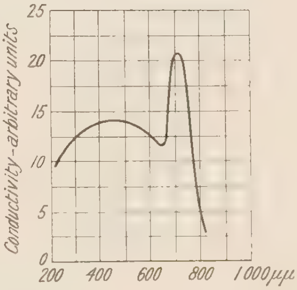


Fig. 22.—The Effect of Light of Different Wave-length on the Electrical Conductivity of Selenium.

J. E. H. Gordon, H. N. Draper and R. J. Moss, P. von Schrott, C. Ries, etc., have shown what an important influence the mode of preparation of the selenium has on its electrical conductivity. R. Marc, and A. Pochettino found that the sensitiveness of selenium for red light is increased by *previous exposure* to white or blue light, but the sensitiveness for blue light is not affected by a previous exposure to red light. P. J. Nicholson found that when the cell is subjected to a steady beam of red light, its conductivity is increased 2·5 times, and the red maximum is almost entirely cut out; when subjected to a beam of green light, the conductivity is increased to about 3 times, and the red maximum and the infra-red sensibilities are slightly reduced. P. J. Nicholson found that with a *limited exposure* of 12·5 seconds, the region in which β is the expression $R=a/\beta$ is nearly 0·5 extends into the ultra-violet as far as 230$\mu\mu$. When the time of illumination was reduced to 10 seconds, a noticeable increase in the value of β followed, with a small shift of the region in which β becomes 1 towards shorter wave-lengths. With the longer illuminations (15 and 20 seconds) the contrary was the result. Finally, with exposure until a steady state was reached, it was found that β was approximately constant and equal to 0·5 throughout the entire spectrum. There appeared, however, to be an appreciable minimum in the value of β about the region 600$\mu\mu$, for here the value found in many sets of readings was about 0·4. F. C. Brown and J. Stebbins found that the resistance, R, of grey crystalline selenium is depressed 0·05 to 0·3 per cent. per atm. by *pressures* p, between 1 and 460 kgrms. per sq. cm.:

p . .	1	59	102	250	333	405	453	496
R . .	113,500	106,900	99,900	74,600	64,300	56,000	51,700	44,600 ohms

The decrease in the resistance of selenium by press. between 0 and 600 atm. is approximately a linear function of the press.; and it is a function of the initial resistance whether the initial resistance be conditioned by press. or temp. The press. effect is due to the selenium itself, and not due to a change in the contact resistance between the electrodes and the selenium, or between parts of the selenium itself. F. Montén found a 0·5 to 2 per cent. per atm. decrease at 3000 atm. While F. C. Brown and J. Stebbins found little or no hysteresis at 450 atm., F. Montén found that the resistance returned to its original value only slowly after the selenium had been subjected to a high compression. F. C. Brown and J. Stebbins observed only a small decrease in the sensitiveness of selenium to light at different press. Thus, the percentage change of resistance due to light with and without the application of press. was in one case 6·92 and 5·77 respectively, in another, 7·70 and 7·11; and in a third, 9·70 and 8·89. F. C. Brown found that with single crystals of selenium, the conductivity in the dark increases about 120 times for an increase of press. of 180 atm., and in light the effect is greater. He succeeded in increasing the conductivity of one crystal about a million times by press., and under these conditions the selenium was not sensitive to light. The hysterises was only slight. The change of conductivity produced by light with press. up to 180 atm. is directly proportional to the conductivity in the dark, so that with a green illumination the percentage increase in conductivity is constant. The press. effect makes it easier for the light to change the conductivity, but the press. does not act except at the point of application. A. Wendt studied this subject. F. C. Brown found that the change produced by *tensile stresses* is not so great as for compressive forces.

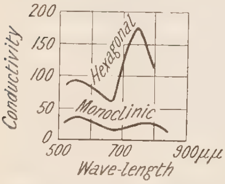


FIG. 23.—Effect of Light of Different Wave-length on the Conductivity of Selenium Crystals.

F. C. Brown and L. P. Sieg found that the effect with a hexagonal crystal prepared by heating vitreous selenium for a couple of weeks at about 200°, and with a monoclinic crystal prepared by heating vitreous selenium in vacuo at 170°, is summarized by Fig. 23. E. O. Dietrich also found that with a high crystallizing temp., selenium gave a maximum at $500\mu\mu$; and when crystallized at a lower temp., the maximum was at $700\mu\mu$. F. C. Brown thus summarized his conclusions: Light of all portions of the visible spectrum alters the conductivity of crystals of metallic selenium of the two systems. When the light is removed the recovery is very rapid. If the entire crystal is illuminated equilibrium is reached in less than 0·2 second. The maximum sensibility for given energy is in the ultra-violet. The crystals are in an equilibrium such that a press. of 180 atmospheres will increase the conductivity a hundredfold. The specific conductivity increases with the applied voltage. The light action may be transmitted almost undiminished throughout the crystal. The press. effect is not transmitted outside the region of the mechanical stress in the crystal. The effect of the electric potential is not transmitted beyond the region of the electrical stress, nor does it manifest itself except in the direction of the electrical field. The absolute sensibility to light increases with press. proportional to the conductivity in the dark. This increased sensibility takes place only at the place where the press. is applied. This increase of sensibility holds for the transmitted light action as well as the direct action of light. The velocity of transmission of the action at a distance by light is greater than two cm. per sec. The crystals of selenium are doubly refracting, and consequently it would be anticipated that the electro-optic properties will be directive by varying when the illumination is along different axis. If the action of light were only on the atoms, irrespective of the crystal structure, the sensibility curves should be the same when different sides of the crystal are illuminated, provided that the reflecting power is constant. F. C. Brown and L. P. Sieg observed that when the illumination is directed on either of the large faces as shown by the arrow, 1, Fig. 24, the sensibility began to increase rapidly at wave-length $0{\cdot}66\mu$, and held a broad maximum with a mean position at $0{\cdot}7\mu$. At

$\lambda=0{\cdot}80\mu$ there was a very large sensibility. By illuminating either of the short edges of the crystal the sensibility had just started to rise at $\lambda=0{\cdot}74\mu$, the position where with side illumination the maximum occurred. In this instance the maximum was very sharp and located at $0{\cdot}79\mu$. In the infra-red beyond wave-length $0{\cdot}82\mu$ this edge of the crystal was more sensitive relatively to the minimum than was the flat surface at its maximum. When either of the longer edges was illuminated as shown by arrow 3, the maximum was at $0{\cdot}76\mu$. R. J. Piersol measured the relation between the light intensity and the photoelectric current. F. C. Brown and L. P. Sieg investigated the effect of varying the angle of incidence on the lamellar crystal of selenium. For angles of about 60°, Fig. 25, there was a decided change in the character of the sensibility curves, but for larger or smaller angles the form of the curve was not changed. With light polarized in the plane of incidence and then at right angles to this plane, there was no change in the character of the sensibility curve, but at about this angle the effect of light polarized in opposite planes was quite different. When the electric vector of the light is perpendicular to the plane of incidence, the sensibility curve was similar to that shown in Fig. 24; but when the electric vector was parallel to the planes of incidence, the maximum was broader and higher. J. C. Pomeroy examined the effect on the transverse conductivity of single crystals.

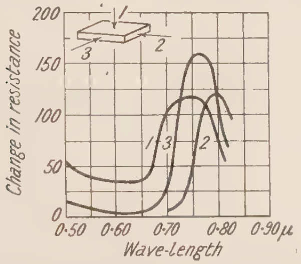


FIG. 24.—The Directive Effect of Light on the Light Sensitivity of Selenium Crystal.

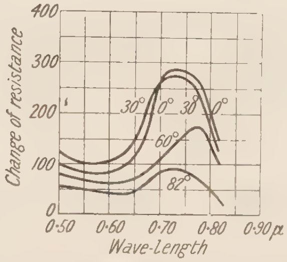


FIG. 25.—The Effect of Polarized Light at Different Angles on the Light Sensitivity of Selenium.

W. G. Adams first showed that the resistance of selenium depends on the impressed *electromotive force*, for he observed that with e.m.f. of 7, 42, and 49 volts, the observed resistances of selenium were respectively 5400, 4600, and 4400 ohms, so that with an increasing voltage the resistance diminishes. Hence, a complete statement of the change in resistance in selenium exposed to light should include the magnitude of the impressed e.m.f. employed in measuring the resistance. F. Kämpf, J. Luterbacher, C. Ries, and L. S. McDowell confirmed this observation. F. Köhler, R. Fürstenau, H. Greinacher, J. J. T. Chabot, L. A. Forssman, R. Sabine, and S. Bidwell, studied this subject. J. Luterbacher's observations on the conductivity of selenium with a direct and an alternating current are illustrated by Fig. 26. E. E. Fournier d'Albe represented the relation between the resistance, R, and the voltage, E, by $(R_1-R)/R_1=a \log E$, where a is a constant varying between 0·1 and 0·5 according to the kind of cell used; and R_1, the resistance when the voltage is unity. J. Luterbacher found that the observed effect is not due to the development of heat; and C. Ries showed that it is not the result of polarization. C. Ries examined the effect of temp. on the voltage effect. If the observations are made when the resistance has attained a constant value the effect is but small up to about 90°, and after that there is an abrupt change. F. C. Brown investigated the effect

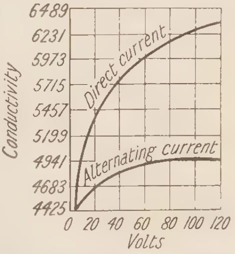


FIG. 26.—The Effect of Impressed Electromotive Force on the Resistance of Selenium.

of press. on the voltage effect—at a low press. raising the voltage from 1·4 to 143 produced a 416 percentage increase in the conductivity, and at a high press. only a 33 percentage increase. C. Ries, and A. Pochettino observed that an increase in the voltage of the current decreases the sensitiveness of selenium to light; and B. Glatzel, and F. C. Brown observed no marked difference, due, according to C. Ries, to the employment of small differences in the impressed e.m.f. or to the use of varieties of selenium which show but a small voltage effect. F. Kämpf found that the sensitiveness of selenium to light, with voltages below 20, is constant, and rapidly decreases with voltages between 20 and 100; and with still higher voltages, the results are anomalous. G. W. White observed that a greater change of conductivity occurs in a selenium block when the ray of incident light is in the direction of flow of the current than when it is at right angles to the current.

The conductivity of the selenium cell varies with the intensity of the light so that if the cell be exposed to intermittent flashes of light of constant intensity a zigzag curve is obtained, Fig. 27, and the dotted lines show that the maximum conductivity in light and the minimum conductivity in darkness soon attain constant values. With many short flashes, the variation of conductivity is proportional to the intensity of the illumination and the time interval. The increase in the electrical conductivity of selenium resulting from illumination is not instantaneous, and the recovery of the original resistance after exposure is, as shown by S. Kalischer, much slower. This phenomenon—the *Nachwirkung* of selenium—is seriously called *inertia, fatigue, lag,* or *hysteresis.* When a cell is illuminated, the greatest decrease in resistance occurs during the first second, but the action is not generally completed until the elapse of 5 or 10 minutes; similarly, the recovery of the original resistance on darkening the cell is not an instantaneous effect, but depends on the duration and intensity of the previous exposure. Some cells require to be kept several hrs. in darkness before the original resistance is recovered, other cells require 2 or 3 days. Working with E. Ruhmer's hard cell, with a resistance, R, in the dark of 100,000 ohms, E. Hausmann found that on sudden illumination:

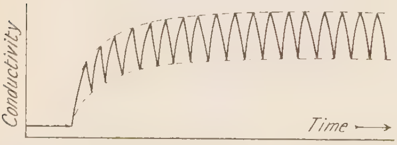


FIG. 27.—Variations on the Conductivity of Selenium with Intermittent Illumination.

Time .	1	2	3	60	120	240	300 secs.
R . .	52,500	42,000	39,000	36,600	35,700	33,000	32,000 ohms

and on sudden darkening:

Time .	0	5	60	120	300	600	1500 secs.
R . .	32,000	45,000	52,500	55,500	60,000	66,000	70,000 ohms

The results are plotted in Fig. 28. M. Bellati and R. Romanese, and O. Majorana found that with intermittent illumination, the resistance of selenium is independent of the frequency of the alternations of darkness and light per second; but B. Glatzel observed that the resistance alters if the ratio of the periods of illumination, t_1, and of darkness, t_3, changes. With continuous illumination, the maximum conductivity is attained more rapidly with strong than with feeble illumination, and this the more, the softer the selenium cell. The recovery of the original conductivity when an illuminated cell is darkened occupies a longer time the greater the intensity of the illumination, and the longer the exposure. B. Glatzel found that the time required for the recovery after an illumination with 1100 luces was 3 times that required for an illumination of 50 luces; and that the time

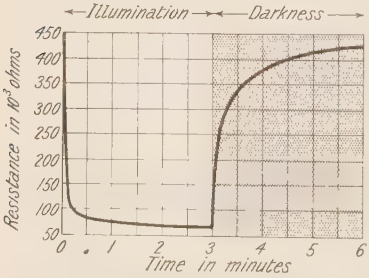


FIG. 28.—The Effect of Illumination and Darkening on the Resistance of Selenium.

required for recovery with a large light energy is proportionally smaller than for a small light energy. According to L. S. McDowell, the form of recovery curve depends on the magnitude of the change of conductivity, and not on the time required for the change. T. Torda obtained the recovery curves shown in Fig. 29 after illuminations occupying respectively 2·5 secs., 10 secs., and 20 secs. According to A. Nisco, the difference between the conductivity values in light and in darkness soon assumes a constant value, and the difference between the highest and lowest values depends on the strength of the illumination. C. Ries made observations on this subject. When light falls on selenium, the conductivity of only the surface layer is raised, but gradually a part of the light is absorbed lower down and thus the conductivity of the selenium below the exposed surface is augmented. Hence the thickness of the selenium exposed to light has an influence on the lag. According to R. Marc, A. Korn, B. Glatzel, N. A. Hesehus, and W. S. Gripenberg, the lag increases proportionally with the *thickness* of the exposed selenium. F. C. Brown found that with selenium 0·11 mm. thick, the light penetrates about 0·014 mm., but all the selenium is conducting and light-sensitive. The effect of filing or sand-blasting is to increase the conductivity. R. Marc calculated that the light penetrates to a depth of 0·00008 mm., and W. S. Gripenberg said that light penetrates 0·05 mm. almost completely. G. W. White concluded that the highest resistance is at the selenium contacts, and that the greatest change by illumination is at the electrodes. F. C. Brown found that with single crystals the action of the light spreads by some sympathetic mechanism throughout the body of the crystal; that the action of light is not at the contacts; that under the influence of press. only the part of the crystal which is under press. is affected; and that under the influence of electrical forces, only the part of the crystal directly under the forces is affected. Hence light has to do with a mechanism essentially different from electrical or mechanical stresses.

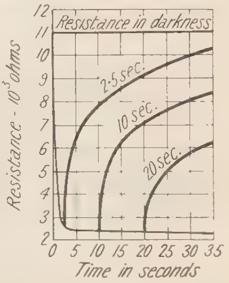


Fig. 29.—Recovery of the Resistance of Illuminated Selenium when Darkened.

The *pre-illumination* of selenium reduces the lag, so that with intermittent illumination the lag finally assumes a constant value, Fig. 30. This subject was investigated by B. Glatzel, C. Ries, and P. J. Nicholson. E. Merritt showed that the recovery of selenium after illumination is slower for shorter exposures; and is more rapid for lower illuminations. He emphasized the resemblance in the behaviour of selenium, as indicated by the change in conductivity, and the behaviour of a phosphorescent substance, as indicated by the intensity of the phosphorescence. E. Hausmann also showed that while the recovery is slower for excitation by the ultra-red than it is for red-light, and slower for red-light than for green-light, the relative times of recovery after exposure to different wave-lengths varies with individual cells. In general, the lag increases with the *wave-length* of the light being greater for red-light than for blue-light. A. H. Pfund, and L. S. McDowell found that the maximum sensitiveness is more rapidly attained in blue-light than in red-light; P. J. Nicholson that the lag in the ultra-red is very marked; and B. Glatzel, that the lag in the greenish-yellow part of the spectrum is less than in red, but for the same effect on the conductivity, the lag is independent of the wave-length of the light. The presence of *impurities* affects the lag. A. Korn obtained the smallest lag by using pure selenium and platinum electrodes, while selenium contaminated with selenides showed considerable lag. B. Glatzel said that a greater lag is obtained with copper electrodes than with platinum electrodes—but the use of different preparations of selenium make the conclusion ambiguous. As indicated above, R. Marc noted that the presence of certain metal salts in the selenium hastened the attainment of equilibrium in light and so abbreviated the lag. B. Glatzel, limiting himself to currents with a comparatively small e.m.f.—10–20 volts—observed that the voltage of the impressed *electromotive force* had no effect on the hysteresis of selenium, but C. Ries showed that increasing the voltage lessened the sensitiveness and also the lag, and that the decrease in the lag is proportionally greater than the decrease in the sensitiveness to light. This is illustrated by Fig. 30. E. H. Kennard and C. Moon studied the photoelectromotive force. L. S. McDowell found that the lag is markedly greater at a low *temperature* than at a high temp. B. Glatzel also observed that the lowering of the temp. from 0° to —70° resulted in an increased sensitiveness and a greater lag. M. Sperling found that the maximum conductivity was attained in 3·5 seconds with a specimen of selenium at —20°, and at 170° in 0·0136 second. The lag was diminished with a rise of temp., and vanishes at 170°. The sensitiveness at 200° was zero.

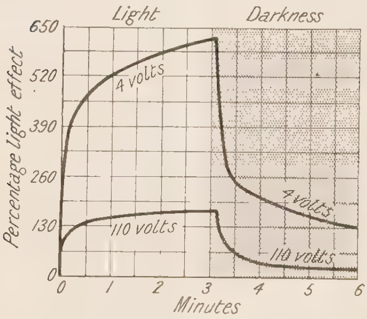


Fig. 30.—The Effect of the Impressed Electromotive Force on the Sensitiveness and Lag of Selenium.

In order to account for the remarkable effect of light on the electrical conductivity of selenium, J. Moser supposed that the light generates heat which improved the contact between the selenium and the electrodes ; M. Sale suggested that the additional conductivity is due to ether waves penetrating between the atoms of selenium so as to increase the conductivity of the whole substance—but this does not explain the effects of hysteresis. S. Bidwell attributed the action to the formation of selenides by the material of the electrodes, but this does not explain the effect with carbon electrodes which form no selenides and give equally good results. O. Weigel's assumption that the decreased resistance of selenium in light is an effect of the adsorbed water, as indicated above, was disproved by C. Ries. The work of C. Berndt, A. H. Pfund, W. von Uljanin, R. Marc, C. Ries, M. Sperling, L. Amaduzzi and M. Padoa, A. Pochettino, G. P. Barnard, R. J. Piersol, etc., makes it highly probable that *the sensitiveness of selenium to light is a specific property of the selenium itself.*

The *allotropic hypothesis* rests on the assumption proposed by E. W. von Siemens, that there are two forms of metallic selenium, one of which is a good conductor, and the other an inferior one. Ordinarily these are in a state of equilibrium, but illumination displaces the equilibrium in favour of the variety with the high conductivity, while in the dark this state is reversed and the normal resistance is eventually restored—*vide supra*, the allotropic forms of selenium. This hypothesis was favoured by G. Berndt, A. H. Pfund, R. Marc, M. Sperling, A. Pochettino, B. Glatzel, H. R. Kruyt, E. Berger, H. Pélabon, and W. Biltz. F. C. Brown assumed that three modifications of selenium are involved. The A-form is supposed to be a non-conductor, the *B*-form a metallic conductor, and the *C*-form has a conductivity negligibly small in comparison with that of the *B*-form. Illumination transforms some *A* into *B*, and *B* into *C*. F. C. Brown later abandoned this hypothesis in favour of the electronic hypothesis. I. A. Kasarnowsky said that the potential of selenium becomes more positive on illumination, so that the difference between illuminated and non-illuminated selenium cannot be ascribed to the formation of a new allotropic modification, and the cause of the photosensibility is not a reversible photochemical reaction.

D. Reichinstein ascribed the light effect to *polarization.* He said that directly a current of voltage E_0 passes through the selenium cell a back e.m.f. or polarization current of E volts is evoked so that the observed effect is $E_0—E$ volts. E is very large, but in light it is diminished, apparently reducing the resistance of the cell. This hypothesis was criticized by H. Greinacher. H. Greinacher observed a certain analogy between the decrease in the resistance of selenium produced by an alternating current and by light. He attributed the differences to the different frequencies, that of light being 5×10^{14}, and that of the currents used by him being

3×10^3. He therefore assumed that the light sensitiveness of selenium is a special case of a general property when the electrical resistance is sensitive to *electromagnetic oscillations* of certain frequencies. In the case of selenium, an increased conductivity is due to the separation of electrons by electromagnetic oscillations; this increase renders more electrons available for carrying the current. The analogy between the effects produced by light and by the alternating current was criticized by C. Ries. A decrease in the resistance of selenium under the influence of electric oscillations was also observed by C. Agostini, and G. Berndt.

In the co-called *Becquerel effect*, discovered by A. C. Becquerel in 1839, if one of the two electrodes dipping in an electrolyte be illuminated, the electrode potential is altered, and an electric current is produced. The photoelectric current flows in the direction of the light rays, and in a selenium cell it is assumed that negative electrons pass from the illuminated layer of selenium to the electrode by a phenomenon analogous to the Becquerel effect. The photoelectric current was found by C. Ries to be produced by the same rays of light as those which augment the conductivity. D. Kordes supposed selenium to be a mixture of good conductivity matrix and bad conductivity crystals, and that light produced a potential between them so that the selenium is in the same state as the glass of a Leyden jar. This produces an e.m.f. which is the cause of the augmented conductivity of an illuminated selenium cell. The phenomenon was studied by R. L. Hanson, who found (i) for the same illumination, the e.m.f. is independent of the current through the cell; (ii) over wide ranges, the e.m.f. is directly proportional to the intensity of illumination; (iii) for the same intensity of illumination, the e.m.f. is a maximum in the region $\lambda=490$.

F. Himstedt assumed that the light rays provoke the fluorescence or phosphorescence of selenium and that the element under the action of its own rays, so to speak, changes its resistance. The phosphorescence could not be proved experimentally, but N. A. Hesehus, and E. Merritt observed a similarity between the effect of light on the conductivity of selenium, and on the intensity of the phosphorescence of zinc sulphide. N. A. Davis and J. J. T. Chabot observed that selenium which has been illuminated can emit rays capable of affecting a photographic plate.

N. A. Hesehus supposed that the light produced a partial dissociation of selenium molecules, and that the conductivity is favoured by the resulting *ionization*. P. von Schrott also said that selenium in darkness has no free ions, and that it is ionized by light so that the free ions favour the conductivity; in darkness the ions recombine to form molecules. L. Amaduzzi supposed that the increase of conductivity in light was produced by a discharge from particle to particle, as in *Hallwach's effect* (*q.v.*); but this phenomenon is most favoured by ultra-violet light, whereas the conductivity is most sensitive to the visible red. A. H. Pfund considered that light absorbed by selenium sets up resonance within the atom, and this, in time, gives rise to an expulsion of electrons—this increasing the number of electrons available for carrying the current, and hence increasing the conductivity.

In the modern *theory of electrons*, metallic conduction consists in the transfer of electrons through the metal, while in liquid conduction, ions or groups of ions are transferred under the guidance of positively charged electrons or protons, in the direction imposed by the electric field of force. In semi-conductors, both processes occur, but since in selenium there is little evidence of the actual transfer of selenium by the current, the conductivity of that element in light is attributed, as in metallic conduction, to free electrons. In good conductors there are supposed to be nearly as many free electrons as there are atoms, while in poor conductors like selenium there are far more atoms than electrons. E. E. Fournier d'Albe said that we are not likely to be far wrong in estimating that normally a selenium tablet an inch square will contain about a million free electrons among its billion selenium atoms, but when intensely illuminated, it may contain ten or hundred times as many electrons as in the dark. How light expels the electron is not known. If the electrons of the atom are revolving in their orbits about the nucleus, under the "gravitational" attraction of its positive charge, an alteration of the electrical field may distort a circular or elliptical orbit into a parabola or hyperbola, and so result in the ejection of an electron. The theory was discussed by A. M. MacMahon.

The work required to ionize an atom, *i.e.* to make an electron leave an atom, with which it is bound, is about 10^{-10} erg; and this work is supplied by the energy of light; and E. E. Fournier d'Albe estimated that there is sufficient energy in the light of a candle, 3 ft. away, to completely ionize 400 billion atoms per second, and all the atoms in the tablet of selenium an inch square and the selenium would acquire the conductivity of copper. As indicated above, Fig. 28, the conductivity of selenium rises rapidly for a second or two when light falls on the element; the conductivity then increases more and more slowly until finally it reaches a constant value. There is therefore an influence opposing the separation of electrons from the atoms. The roving electrons, however, meet atoms which have lost their electrons and the electrons return to the atoms. The greater the proportion of electrons, the greater the proportion of positively charged atoms, and the more likely is combination to occur. E. E. Fournier d'Albe showed that the decrease in the number of ions, produced by the action of light on selenium, is proportional to the number of ions already present—double the number of ions of one kind; and the chances of recombination in a given time would be double; and double the number of both kinds, and the chances of recombination would be doubled again, *i.e.* quadrupled. When the light is cut off from selenium the conductivity falls off rapidly, though not so rapidly as it rose, Fig. 31, and eventually returns to its normal value. This means, in the language of the electron theory, that the electrons at first very numerous have many chances of uniting with the unmated atoms, but as time goes on, the electrons occupy a longer and longer time to find their destined companions. When light waves fall on selenium, they penetrate only a small distance, and the number of electrons liberated will be proportional to the intensity of the light, but the rate of recombination of the electrons is the same whether the selenium is illuminated or not, for it is determined by the proportion of ions present, being proportional to the square of the number of ions present. It therefore increases rapidly as ionization proceeds. In a short time, when the selenium has attained its maximum conductivity, the number of ions formed by light is equal to the number which recombine in the same time. The energy of the light will then be proportional to the square of the number of ions formed; that is, the current produced by light will be proportional to the square root of the illumination. E. E. Fournier d'Albe found this rule applicable for light so faint as to be equivalent to the light from a single star; and he added that if any one were to strike a match on the moon, it would be possible, by means of selenium, to discover the fact on earth, without the aid of a telescope, and in one second of time. According to the quantum theory, no ionization can occur if the available energy is less than one quantum, $5{\cdot}2\times10^{-11}$ erg, but the eye is so sensitive that E. E. Fournier d'Albe estimated that it can detect amounts of light as small as 400 quanta falling on the retina per second.

E. E. Fournier d'Albe represented the recovery curve for selenium after illumination by $N^{-1}-N_1^{-1}=at$, where a is a constant; N, the number of electrons set free by light; and N_1 the number of electrons at the time t; and the action of light, $dN/dt=C-aN^2$, where C is proportional to the intensity of the incident light. When integrated for N, there follows $N=(C/a)^{\frac{1}{2}}\tanh(tC^{\frac{1}{2}})$, an equation which represents the action on selenium in the given circumstances.

The electron theory has been also discussed by C. Ries, F. C. Brown, W. Späth, F. Kämpf, and others. Some of these theories—*e.g.* the theory of electrons—do not exclude the allotropic hypothesis. They may supplement one another. W. del Regno, however, said that the effect is purely electronic, and is not due to any chemical transformation of one allotropic form into another; and I. A. Kasarnowsky showed that the potential of selenium always becomes more positive on illumination, and it is hence inferred that the photosensibility is not a reversible photochemical reaction between two allotropic forms of selenium.

C. Ries found that some selenium preparations are strongly hygroscopic, and when damp, show a strong **polarization current** when used with a continuous current. When a specimen is dried it shows scarcely a trace of polarization, but on exposure to the atmosphere, it again shows polarization. Cells made by crystallization from heated selenium do not show polarization effects, and they possess a higher sp. resistance than when moist selenium is used. A moist selenium cell, when illuminated, thus behaves like an electrolytic cell. A. O. Rankine and J. W. Avery found that the polarization or secondary e.m.f. displayed by selenium cells, and the abnormal effect of illumination on the corresponding secondary currents, are probably due to an invisible water-film in parallel with the selenium because the polarization disappears almost completely with prolonged drying. S. Kasarnowsky gave —0·77 volt for the normal potential of $Se'' \rightarrow Se$ metal. W. G. Adams and R. E. Day observed a current, resembling in some respects the polarization current, with selenium between two platinum electrodes, and A. Pochettino named it a **secondary current.** It is not due to moisture. Unlike the polarization current, the effect is more marked the greater the resistance of the cell; and unlike the polarization current, it is most marked in cells whose conductivity increases in light. The e.m.f. of the secondary current is proportional to the e.m.f. of the primary current, and to the sq. root of the time. It is strongest with iron or zinc electrodes, and it is not a thermoelectric phenomenon. Some selenium preparations show **unipolar conduction,** and they can be employed as **rectifiers of alternating currents.** A. H. Pfund, C. Ries, and R. Furstenau observed no sign of polarization or secondary current, or of unipolar conduction with thoroughly dried selenium cells. O. Weigel said that unipolar conduction is not a specific property of selenium, but is conditional by the presence of moisture in the pores of selenium *en masse*. The rectifying action of selenium cells was studied by H. Greinacher and C. W. Miller, A. Pochettino, and C. Ries. H. Greinacher emphasized the analogy between the effect of the amperage of the alternating current on the change in resistance, and the intensity of the illumination on the resistance. R. Fürstenau showed that the selenium cells used by H. Greinacher were anomalous, and C. Ries showed that the analogy is not characteristic of selenium. R. de L. Kronig found that the increase in conductivity, δK, with current, C, and voltage, E, due to electronic bombardment, is in accord with $\delta K/K=(1+98{\cdot}5EC)^{\frac{1}{2}}+1$ derived from the electronic theory.

C. Agostini, G. Berndt, and L. S. McDowell found that *electrical oscillations* lessen the resistance and increase the sensibility of the selenium cell; but E. F. Perreau, and A. Massini obtained only negative results. L. Amaduzzi observed a change in the resistance of selenium when it is exposed in a strong *magnetic field*, and assumed that selenium shows a negative Hall's effect. A. D. Udden found that the **ionizing potential** of selenium vapour is 12·7 volts; and if this value be substituted for V in the equation $v=Ve/h$, the limiting frequency of the spectrum of selenium vapours is about 980 A. E. F. Perreau, and J. W. Giltay found that the resistance of selenium is lowered by exposure to *X-rays* much in the same way as it is by illumination; and G. Athanasiadis represented the relation between the conductivity, K, and the intensity, I, of the X-rays by $I=k(K-a)b$, where a and b are constants. Observations were also made by R. Fürstenau, F. Himstedt, R. Mayer, and M. Meyer. H. Küstner studied the sensitiveness of the selenium cell to X-rays of different wave-lengths. L. Bloch found that while the resistance of selenium was 30,100 ohms in darkness, and 900 ohms in different daylight, it reached 800 ohms when protected by black paper and exposed to *radium rays*. The resistance recovered very slowly when removed from the influence of these rays. F. C. Brown and J. Stebbins found that under the influence of *β-rays*, the resistance of selenium decreased 30 per cent., and that the recovery from the exposure occupies 5 times longer than for a light exposure of short duration. A. M. McMahon also studied the action of X-rays, and gamma rays on the electrical conductivity of single crystals. R. de Kronig studied the effect of electronic bombardment on the conductivity of selenium. W. del Regno found a marked variation in the resistance of a cell exposed to mesothorium radiation near-by; but when the distance is increased, the sensitiveness diminishes so that the sensitiveness of the cell varies with the distance between the cell and the mesothorium, and with the duration of the excitation. If the excitation is not too intense, a relatively short time suffices for the cell to recover conditions of sensitiveness almost identical with those preceding the excitation. With alternate equal periods of excitation and rest, the cell exhibits, after the first few cycles, an almost constant variation in the resistance, so that a single excitation is insufficient to indicate the time taken by the selenium to recover its original sensitiveness after excitation.

E. Obach, F. Himstedt, and F. Bonola and G. Cavino found that the resistance of selenium was lowered by exposure to **phosphorescent light** from barium carbonate, etc. E. van Aubel exposed a piece of selenium, of resistance 496,000 ohms, at a distance of about 3 cms. from the surface of hydrogen dioxide for three or four minutes, and the resistance decreased to 324,000 ohms. When similarly exposed for fifteen minutes to turpentine, the resistance diminished from 461,000 ohms to 386,000 ohms. As light, radium rays, and X-rays produce a similar diminution of the resistance of selenium, the experiments seem to show that hydrogen dioxide and turpentine emit rays. The resistance of selenium was also diminished by exposure to ozone, and by caoutchouc or camphor which had been exposed to ozone. A. B. Griffiths found that when a piece of selenium was exposed at a distance of 5 cms. from an alcoholic soln. of the pigment from geranium petals for about 15 minutes, its electrical resistance fell from 462,000 ohms to 320,000 ohms. Similar results were obtained with other vegetable and animal pigments. O. Dony-Hénault also studied the effect of hydrogen dioxide on the resistance of selenium; and C. Ries showed that many of the results attributed to different agents are really effects of moisture. J. J. T. Chabot said that a selenium cell sent out radiations capable of effecting a photographic plate, but G. Berndt could not confirm this.

There are two types of **galvanic selenium cells**—electrolytic, and solid. R. Sabine first made the electrolytic cell by coating a metal plate with selenium on one side, varnishing it on the other side, and placing it opposite another plate in an electrolyte. G. M. Minchin improved this kind of cell by coating the flat end of an aluminium wire with selenium, enclosed it in a glass tube open at both ends, and immersed it in a soln. of œnanthol opposite a platinum wire. When one electrode is illuminated, a photoelectric current is developed in the direction of the path of the light rays, and flows in the electrolyte from the darkened to the illuminated electrode. Hence, the illuminated electrode becomes more electronegative. In the ordinary selenium cell, the effect is due to a change in the conductivity of the selenium, here a definite electromotive force is developed. With a steady illumination, the effect is not usually constant, but decreases at first rapidly, and then slowly, so that finally the e.m.f. attains the value it had in darkness. The polarization and other properties of these cells were studied by C. Ries, M. Reinganum, B. Glatzel, and H. Pélabon. V. P. Barton observed the maximum at about 5700 A. The effect is positive, and proportional to the intensity to the power of two-thirds, $I^{\frac{2}{3}}$.

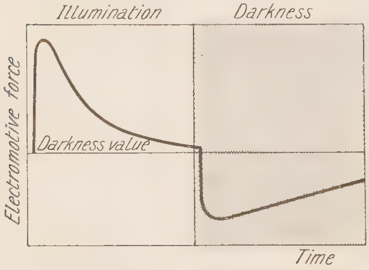


Fig. 31.—The Effect of Illuminating One Electrode of an Electrolytic Selenium Cell.

Solid galvanic cells are obtained by melting a thin layer of selenium between two glass plates each covered with a thin film of platinum—platinum mirror—in contact with the selenium. The selenium may be crystallized or vitreous. W. G. Adams and R. E. Day first prepared these cells, and observed that when the selenium is illuminated an e.m.f. is developed. These cells were studied by S. Kalischer, C. E. Fritts, W. von Uljanin, C. Ries, A. Righi, J. W. Clark, and A. Pochettino. W. von Uljanin obtained from such a cell in sunlight a current of 0·12 volt and $1{\cdot}6\times10^{-5}$ amp.

M. le Blanc[15] found that when used in the form of a thin film on a platinum wire as cathode in a soln. of potassium hydroxide, selenium passes into soln. as polyselenide, Se''_n, where n may be 4·4. In 0·1N-KOH, selenium, according to E. Müller and R. Nowakowsky, passes into soln. with a valency of 0·67–0·75; and the potential at which soln. begins is 0·804 volt against the 0·1N-calomel electrode. According to E. Müller, no cathode **deposition potential** could be observed for selenium from selenious acid, although selenium was seen to be deposited at about 0·05 volt, but the first selenium deposited appears to act as an insulating diaphragm and prevents further deposition; when the voltage is raised so that hydrogen is liberated, the selenium leaves the electrode in flakes. On adding copper sulphate to the sulphuric acid soln. of selenious acid, the selenium and copper are deposited together in a conducting form at +0·15 volt, so that all the selenium may be deposited at this potential. Selenium cannot be electrolytically deposited from selenic acid on platinum either at 20° or 80°. A. Jilek and J. Lukas studied the electrodeposition of selenium; and A. Rosenheim and M. Pritze, some complex selenium anions. E. Berger said that the **electrode potential** of selenium in a 0·3 per cent. soln. of sodium selenide is —0·05 volt, and is independent of the previous history of the selenium. A. Günther-Schulze studied the cathodic spluttering of selenium. F. Heinrich[16] found the **electromotive force** of the cell Se | M-H_2SO_3 and a normal electrode at 18° was +0·461 after one minute and +0·442 after 20 hrs.; and after the addition of a little potassium iodide and sulphuric acid, 0·389 volt after one minute and 0·424 volt after 46 hrs. The e.m.f. of the cell Se | M-H_2SeO_3, M-H_2SO_4 with a normal electrode is —0·451 volt after one minute and —0·471 after an hour; Se | M-H_2SeO_3, M-KOH, —0·020 volt after 2 minutes, and —0·012 volt after 18 hrs.; Se | M-Na_2SeO_3, M-H_2SO_4, —0·322 volt after one minute, and —0·426 volt after $3\frac{2}{3}$ hrs.; and with 0·1M-H_2SO_4, —0·322 volt after a minute, and —0·258 volt after $2\frac{1}{3}$ hrs. the cell Se | M-H_2SeO_4 and a normal electrode, had an e.m.f. of —0·510 volt after one minute, and —0·4756 after $18\frac{1}{2}$ hrs.; Se | M-H_2SeO_4, M-H_2SO_4 and a normal electrode, —0·583 volt after 2 minutes, and —0·513 volt after 48 hrs.; Se | M-H_2SeO_4, M-NaOH, and a normal electrode, —3·363 volt after 2 minutes, and —0·471 after 28 hrs.; Se | M-Na_2SeO_4, M-H_2SO_4 and a normal electrode —0·297 volt after one minute and —0·372 volt after one hour; and with 0·1M-H_2SO_4, —0·346 volt after one minute, and —0·384 after 24 hrs. The potential at which selenium separates from selenious acid—**reduction potential**—is about +0·2 volt at 18°, with selenic acid, 0·15–0·18 volt; and for the reduction of SeO''_4 to SeO''_3 —0·412 volt. H. F. Schott and co-workers found the reduction potential of black selenium to be —0·740 volt. I. A. Kasarnowsky found that in the electrolysis of a 0·0012N-soln. of potassium polyselenide, the selenium electrode had a potential of 0·404 volt at 0·4 hr., and this rose to a maximum of 0·429 volt after 17 hrs., and then fell to 0·398 volt after 42·3 hrs. M. le Blanc gave S, Se, Te, As, and Sb for the order in which electrodes of the elements are affected. E. H. Kennard and E. Moon studied the effect of illumination on the contact potential of selenium. F. W. Bergstrom gave for the electronegative series in liquid ammonia: Pb, Bi, Sn, Sb, As, P, Te, Se, S, and I. S. R. Carter and co-workers found that the system SeO_2–Se in conc. sulphuric acid gives a reproducible oxidation potential which is not affected by light. Ten-fold changes in conc. produce a change of 0·022–0·028 volt. It is assumed that selenium tetrachloride is formed as an intermediate step, and yields $Se^{\cdot\cdot\cdot\cdot}$-ions.

A. L. Hughes[17] found that selenium exhibits the **photoelectric effect** giving off photoelectrons when illuminated by the light from a mercury lamp. The phenomenon was studied by G. C. Schmidt, F. C. Brown, G. Zoltan, R. L. Hanson, and C. Ries. A. L. Hughes said that selenium becomes a conductor when illuminated by visible light and yet the photoelectric effect sets in only when the wave-length is less than λ=2200 B.; V. P. Barton gave 2260 A. This is in agreement with the fact that the escape of photoelectrons from the surface of many non-metallic substances requires light of shorter wave-length than is necessary to produce the increased conductivity; meaning that the long wave-length limit for the conductivity effect is farther towards the red than the photoelectric effect. C. Carpini found the photoelectric effect to be 0·247–0·32 at 8°, and 0·07 at 96°, making the temp. coeff. 0·0025. At the temp. of liquid air, the photoelectric effect is very slight, but it can be detected. W. del Regno could detect no difference in the photoelectric emission in the dark and under the influence of light, and inferred that free electrons played no part in the phenomenon. R. Bär made estimates of the elementary quantum from measurements on the sub-microscopic particles of selenium. R. Hamer found that the photoelectric effect occurs with light of wave-length over 2050 A. B. Gudden and R. Pohl, R. M. Holmes and N. L. Walbridge, and K. Scharf studied this subject. W. E. Tisdale examined the effect of gases on the photoelectric properties. W. Gerlach observed that with thin plates of selenium, the negative radiometer effect becomes positive if the red and ultra-violet rays, for which the substance is transparent, are cut off. C. E. S. Phillips found that the electrical resistance of selenium is rapidly decreased by exposure to cathode rays; and the effect is not due to the production of X-rays.

A. Matthiessen[18] observed that selenium had the extraordinarily high value of 805 microvolts for its **thermoelectric force** against platinum at 20°; and W. G. Adams and R. E. Day said that the position of selenium in the thermoelectric series depends on its annealing time and temp. In any case, S. Bidwell showed that if moisture be excluded, the current always flows from the platinum to the selenium; and R. Blondlot showed that the current flows in the selenium circuit, from the hot to the cold junction. F. Weidert gave 1129 microvolts for the thermoelectric force of metallic selenium against platinum. R. M. Holmes and A. B. Rooney gave $E=1\cdot1\theta+0\cdot00017\theta^2$ for the thermal e.m.f. in millivolts between 0° and 180°, of selenium and copper. A. Righi observed that the thermoelectric force of selenium between lead electrodes is 0·506 microvolt, and the thermoelectric force increases linearly with temp. up to the m.p. F. Weidert gave 1130 microvolts for the thermoelectric force of lead and metallic selenium; while H. Pélabon observed that selenium forms good thermocouples with antimony alloys and with tin alloys. F. Weidert observed that the thermoelectric force decreases 3–4 per cent. when it is illuminated. R. M. Holmes observed that illumination causes a decrease of about 5 per cent. in the thermoelectric power of selenium, corresponding with a five-fold increase in conductivity. The effect is explained by assuming that a decrease in the potential energies of electrons in the interatomic space causes an increase in the mean free path of conducting electrons. A large thermal e.m.f. is developed in a circuit formed entirely of selenium homogeneous in every respect except that a region of temp. gradient of one sign is illuminated, whilst that of the other sign is in darkness; the illuminated selenium is positive at the cold junction; D. Todesco studied the effect of light on the thermoelectric current. E. H. Hall studied the Thomson effect; and W. Ogawa, the rectifying action on the electric current.

According to P. A. Bonsdorff,[19] T. Seebeck, and P. Riess, selenium becomes electrically negative when rubbed in dry air. E. T. Wherry said that crystals of selenium are poor radio-detectors; and I. Stransky discussed the rectifying action of the selenides; and E. Merritt studied the effect of light on selenium rectifiers. O. U. Vonwiller gave 6·13 for the **dielectric constant** of vitreous selenium with $\lambda=\infty$; and W. Schmidt, 6·60 for λ=75. W. Späth found the change in the dielectric capacity of selenium with illumination runs parallel with the change in conductivity. S. Kyropoulos gave 7·39 at 21·7°. G. L. Addenbrook[20] studied the relation between the dielectric constant and the other physical properties of selenium. K. Honda found the **magnetic susceptibility** of selenium to be $-0{\cdot}32\times10^{-6}$ mass units at 18°, and P. Curie $-0{\cdot}31\times10^{-6}$ at 20°–415°; K. Honda, and T. Soné gave $-0{\cdot}304\times10^{-6}$, and M. Owen, $-0{\cdot}32\times10^{-6}$ for fused selenium. J. Königsberger gave $-0{\cdot}50\times10^{-6}$ vol. units for red selenium, and $-1{\cdot}3\times10^{-6}$ for vitreous selenium. S. Meyer gave $-0{\cdot}001\times10^{-6}$ for the **atomic magnetism.** P. Pascal gave -235×10^{-7} for the **atomic susceptibility** ; and S. S. Bhatnagar and C. L. Dhawan, $25{\cdot}4\times10^{-6}$. F. Ehrenhaft and E. Wasser studied the magnetic susceptibility of selenium ; and A. Dauvillier, the dimagnetism and atomic structure of selenium. C. W. Heaps found that the magnetic susceptibility is not affected by insolation.

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§ 5. The Chemical Properties of Selenium

Selenium behaves very like sulphur in many of its reactions, but the compounds formed with selenium are less stable than those formed with sulphur. Soln. of the alkali selenides, for instance, are decomposed by air with the separation of selenium ; selenic acid is decomposed by hydrochloric acid with the separation of selenium—sulphuric acid under similar conditions is stable. Selenium dioxide acts as an oxidizing agent on ferrous, chromous, and stannous salts—sulphur dioxide, on the other hand, reduces ferric to ferrous salts, etc. A. von Bartel attributed the marked difference between the stability of several sulphur compounds and that of the corresponding selenium derivatives to the preference which selenium exhibits for existing as a quadrivalent element, whereas sulphur exists rather as a bi- or sexa-valent element ; selenium should therefore not be classed with sulphur, but rather with tellurium which it more closely resembles.

W. Ramsay and J. N. Collie,[1] and W. T. Cooke observed no evidence of combination between heated selenium and **helium ;** and W. T. Cooke, none with **argon.** Selenium unites directly with **hydrogen** under the influence of heat, forming hydrogen selenide. A. Ditte said that above and below the range 250°–520°, the selenide is disassociated—*vide infra*, hydrogen selenide. According to J. Papish, when selenium dioxide is introduced into the hydrogen-air flame, it produces a deep blue luminescence in the inner zone, pale blue in the middle zone, and green in the outer zone. There is a deposition of selenium in the inner and middle zones, but no deposition in the outer zone. Hydrogen selenide produces a very faint blue luminescence in the inner zone, deep blue in the middle zone, and green in the outer zone. There is a deposition of selenium in the inner zone, but no deposition elsewhere. Selenium produces a luminescence coloured blue, violet, and green in the inner, middle, and outer zones respectively ; in this case and in all following cases, the element is deposited in the inner and middle zones, but there is no deposition in the outer zone. H. B. Weiser and A. Garrison observed the flame reaction of selenium ; selenic salt produces a blue luminescence, which is the most characteristic in flames containing selenium. It is probable that this luminescence is due chiefly to the reaction from selenic ion to non-ionized selenic salt. A red luminescence may occur in flames containing selenium, and it is usually less intense than the blue luminescence. The red coloration is due in part to the colour of the vapour, in part to a purely thermal luminescence, and in part to some stage of the chemical reaction from the vapour of the element to the quadrivalent ion. A green tip in the flames in air charged with a selenium compound is not a luminescence, but is due to the green colour of the vapour of the dioxide, which appears greener by reflecting the blue luminescence just below. Selenium was found by J. J. Berzelius, and by F. Krafft and O. Steiner to have a smaller affinity than sulphur for **oxygen.** J. J. Berzelius said that when gently heated in **air,** it sublimes without change, and when more strongly heated—*e.g.* by contact with flame—it burns with a reddish-blue flame; and it burns in oxygen with a flame which is white below, and bluish-green above, and it is converted, at least partially, into selenium dioxide and trioxide. It remains unaltered by oxygen in the cold. A. Mailfert observed that **ozone,** in the presence of moisture, converts selenium into selenic, not selenious, acid. C. F. Cross and A. Higgen found selenium exerts an inappreciable action on **water** at 160°. H. O. Schultz's soluble form is colloidal selenium (*q.v.*). J. Jannek found that selenium is completely insoluble in water. C. Ries has discussed the action of moisture in reducing the conductivity of illuminated selenium—*vide supra.* L. J. Thénard, and H. Fonzes-Diacon found that **hydrogen dioxide** dissolves finely divided selenium, forming selenic acid. The action of hydrogen dioxide in modifying the conductivity of selenium, previously indicated, was discussed by E. van Aubel, and O. Dony-Hénault.

H. Moissan observed that selenium unites directly with **fluorine** in the cold giving off white fumes, and finally the selenium takes fire, forming a white, crystalline fluoride (*q.v.*). J. J. Berzelius found that when **chlorine** is passed over selenium, the solid melts with the evolution of heat, forming a brown liquid, selenium monochloride, which then forms a white solid, selenium tetrachloride (*q.v.*). O. and C. A. Silberrad found that in addition to acting catalytically as a chlorine carrier in the chlorination of toluene by sulphuryl chloride, selenium also acts similarly in the direct chlorination of toluene by chlorine both in the presence and absence of light. Just as with sulphuryl chloride, it accelerates substitution in the nucleus and decreases it in the side-chain. According to G. S. Sérullas, selenium and **bromine** are miscible in various proportions; bromine rapidly combines with powdered selenium, and the reaction is attended by a hissing noise, and the evolution of heat. The mixture solidifies to a brownish-red mass of the monobromide (*q.v.*). J. B. Trommsdorff said that when selenium is heated with an eq. proportion of **iodine,** the mixture forms a dark grey mass from which alcohol extracts all the iodine. P. Guyot said that a soln. of selenium in carbon disulphide reacts with iodine, forming selenium moniodide. W. Engelhardt observed that colloidal selenium reacts slowly with a soln. of iodine and potassium iodide. According to J. J. Berzelius, and A. C. Schultz-Sellack, selenium is not attacked by **hydrochloric acid.** According to S. R. Carter and co-workers, red amorphous selenium does not dissolve appreciably in conc. hydrochloric acid during 3 days' contact at 20°, even though the liquid be in contact with air. If selenium dioxide be present, the selenium dissolves. The solubility of selenium in $0{\cdot}1M\text{-SeO}_2$ and $11{\cdot}6N\text{-HCl}$ is 1·35 grms. per litre (within 5 per cent.). The solubility of selenium falls off rapidly with diminishing conc. of acid, and, on dilution of sat. soln. with water, the red amorphous selenium is precipitated. P. Hautefeuille said that **hydriodic acid** acts on selenium as it does on sulphur; when the two are heated in a sealed tube, hydrogen selenide and iodine are formed, and on cooling the reaction is reversed—selenium and hydrogen iodide are reproduced. L. Rolla studied the reaction: $2HI+Se \rightleftharpoons H_2Se+I_2$.

Selenium unites with **sulphur,** forming sulphides (*q.v.*). J. J. Berzelius, and B. Rathke said that the two elements may be fused together in all proportions. H. Moissan and P. Lebeau found that when heated, selenium decomposes **sulphur hexafluoride;** and, according to F. Krafft and O. Steiner, **sulphur monochloride.** The latter reaction, said M. Berthelot, is in agreement with the thermal data:

$2Se_{amorphous}+Cl_2=Se_2Cl_2+22{\cdot}15$ Cals.; and $2Se_{rhombic}+Cl_2=Se_2Cl_2+17{\cdot}66$ Cals. V. Lenher and H. B. North observed that **thionyl chloride** has but little action on selenium at ordinary temp., but when heated, the reaction is symbolized: $2SOCl_2+Se=SeCl_4+SO_2+S$; the element is rapidly attacked by **sulphuryl chloride** with the evolution of heat and the formation of sulphur dioxide and selenium tetrachloride: $2SO_2Cl_2+Se=SeCl_4+2SO_2$. W. Prandtl and P. Borinsky found that with an excess of **pyrosulphuryl chloride** at 120°–140°, a mixed oxytetrachloride is formed. L. A. Tschugaeff and W. G. Chlopin found that selenium forms sodium selenide when treated with **sodium hyposulphite,** sulphur under similar conditions is only slightly attacked. C. Sandonnini found that when selenium acts on potassium or ammonium **hydrosulphite,** the total reaction may be expressed by the equation: $4MHSO_3\rightarrow 2M_2SO_4+SO_2+S+2H_2O$. This probably takes place in the three stages, (1) $M_2SO_3+Se\rightarrow M_2SSeO_3$, (2) $M_2SSeO_3+M_2SO_3+2H_2SO_3\rightarrow M_2SO_4+M_2S_3O_6+Se+2H_2O$, and (3) $M_2S_3O_6\rightarrow M_2SO_4+SO_2+S$. Thus, the true catalytic action of the selenium would cease when only one-half of the total sulphuric acid is formed. It is found that, when reprecipitation of the selenium occurs, the quantity of sulphuric acid does not correspond with one-half the final amount, and that the final amount is in excess of that indicated by those equations. These divergences may be attributable to the facts that the end of the initial phase cannot be gauged exactly, that the reactions become superposed, and that the excess of sulphur dioxide undergoes partial oxidation. The quantity of sulphur which separates and that of sulphur dioxide not participating in the reaction do not, indeed, correspond exactly with those calculable from the above reactions. It is possible also that secondary reactions lead to the formation first of selenothionate and thiosulphate, and afterwards of other polythionates, and that the formation and subsequent decomposition of these compounds give rise to the divergencies mentioned above. B. Rathke and H. Zschiesche found that selenium is insoluble in a soln. of **barium sulphite,** but 100 parts of **potassium sulphite** in aq. soln. dissolve 28·95 parts of selenium; and 100 parts of **magnesium sulphite** in aq. soln. 32·35 parts. H. Uelsmann found that red selenium dissolves in a soln. of **ammonium sulphite.** F. Krafft and O. Steiner, however, found that when selenium dioxide is heated in a sealed tube with sulphur at 110°, sulphur dioxide is formed. R. Weber found that selenium dissolves in liquid **sulphur trioxide,** forming $SeSO_3$; and G. Magnus said that all the forms of selenium yield green soln. with **sulphuric acid**—*vide infra.* A. C. Schultz-Sellack also observed the solubility of selenium in forming sulphuric acid. Selenium dissolved in sulphuric acid is precipitated by the addition of water, and N. W. Fischer said that when the soln. is boiled, sulphur dioxide is evolved, and selenious acid is formed. A. Hilger added that a very conc. soln. of selenium does not evolve sulphur dioxide, but does so after the addition of more acid. R. H. Adie observed that when sulphuric acid and selenium are heated together sulphur dioxide, but no hydrogen sulphide, appears at 170°. According to R. Auerbach, the metalloid selenium dissolves in **pyrosulphuric acid** as diatomic molecules; and at 130°, it changes into the metallic form and is then present as monatomic molecules, and the green soln. becomes yellow. By the addition of water to soln. of Se_2 in pyrosulphuric acid, with consequent increase in the particle size, at 20° the colour passes from green through yellow and red to violet, and the metalloid is then precipitated, whilst above 130° the colour change is from yellow, through red, to blue and the metallic form is deposited. If, however, the yellow metallic soln. is coagulated at the ordinary temp., the first result is the re-formation of the Se_2 molecules accompanied by the change from yellow to green, *i.e.* in opposition to the colour-dispersity rule. After this, the colour changes proceed in the normal manner, and finally the metalloid is precipitated. M. G. Levi and co-workers found that a soln. of **potassium persulphate** dissolves selenium. W. Prandtl and P. Borinsky represented the reaction with **pyrosulphuryl chloride:** $Se+2S_2O_5Cl_2=SO_3SeCl_4+2SO_2+SO_3$. S. Littmann studied the action of selenium in the manufacture of sulphuric acid (*q.v.*). E. Moles found that the electrical conductivity of sulphuric acid is not affected by selenium, and that its effect on the f.p. agrees with the formation of a polymeric form of $SeSO_5$. R. Auerbach studied soln. of selenium in **pyrosulphuric acid**—*vide infra*, oxysulphates. I. Pouget found that selenium is soluble in soln. of the **alkali sulphides.** H. Pélabon, and A. Ditte found that molten selenium absorbs much **hydrogen selenide,** and on cooling gives it off with "spitting." If some selenium, heated in hydrogen in a sealed tube, is powdered under water, and the latter is rapidly filtered and then exposed to the air, it becomes red, owing to the separation of selenium by the action of the oxygen of the air on the dissolved hydrogen selenide. B. Rathke found that vitreous or metallic selenium is very soluble in **selenium monochloride,** and R. Schneider found that **selenium monobromide** dissolves 22 per cent. of selenium.

According to F. Wöhler, selenium combines indirectly with **nitrogen** to form a nitride, NSe, studied by R. Espenschied, and A. Verneuil. According to J. J. Berzelius, and A. C. Schultz-Sellack, selenium is easily oxidized to selenium dioxide by **nitric acid,** and by **aqua regia.** C. C. Palit and N. R. Dhar said that 13 per cent. nitric acid has no action on selenium, and that 26 per cent. acid exerts but a slight action in 3 hrs. J. J. Berzelius found that neither gaseous **ammonia** nor the aq. soln. has any action on selenium, but G. Calcagni said that an aq. soln. of **ammonia,** sp. gr. 0·888, slowly dissolves a very small proportion of selenium. E. C. Franklin and C. A. Kraus reported that vitreous selenium is soluble in liquid ammonia at 25°, but G. Gore, and C. Hugot found that it is insoluble between −30° and 10°, and C. Hugot attributes E. C. Franklin and C. A. Kraus's result to the use of impure selenium and incompletely dried ammonia. F. W. Bergstrom showed that selenium, at −33° or at ordinary temp., reacts with **potassium amide,** forming a white precipitate which contains an explosive substance; if the selenium be in excess, highly coloured polyselenides are then formed and a soluble, non-explosive *potassium selenoamide.* For the reducing action of **hydroxylamine salts** and of **hydrazine salts,** *vide supra.* J. Meyer observed that both crystalline and amorphous selenium are soluble to a considerable extent in a conc. soln. of hydrazine hydrate. Selenium and **phosphorus** are miscible in all proportions in the fused state, and selenides are formed (*q.v.*). According to F. W. Bergstrom, selenium in liquid ammonia soln. slowly attacks **arsenic.** J. J. Berzelius found that molten selenium dissolves arsenic, forming a selenide (*q.v.*); similarly with **antimony**; and, according to F. Rössler, with **bismuth.** F. Jones found that selenium has no action on **arsine** in the dark and at 100°, but a reaction occurs in sunlight; **stibine** slowly reacts with selenium in the dark at ordinary temp. or at 100°, and a reaction readily occurs in sunlight.

The union of selenium with **carbon,** forming carbon selenides (*q.v.*), is effected indirectly, *e.g.* A. von Bartal obtained a selenide, $C_9Se_4Br_2$, by heating selenium with **carbon tetrabromide,** but H. V. A. Briscoe and co-workers could not verify this—only the mono- and tetrabromides, and a mixture of carbon and selenium was formed. H. V. A. Briscoe and J. B. Peel discussed the action of selenium on **acetylene** which results in the formation of selenophen, C_4H_4Se. A. Besson found that **carbonyl chloride** at 230° forms selenium chloride. According to E. Mitscherlich, 100 parts of **carbon disulphide** dissolve 0·5 part of vitreous selenium at 46·6°, and 0·016 part at 0°. C. F. Rammelsberg obtained results ranging from 0·0267 to 0·0727 part of selenium per 100 parts of solvent at 20°, and E. Mitscherlich said that when vitreous selenium has been some weeks in contact with carbon disulphide, it forms crystalline, red selenium which is less easily dissolved by that menstruum than before. A similar result was obtained by R. Schneider and A. P. Saunders. The latter stated that the action of light increases the solubility of selenium. E. Petersen added that vitreous selenium which has not been pre-heated or annealed is completely soluble in carbon disulphide at ordinary temp., but if it has been warmed, or treated with warm carbon disulphide, part becomes insoluble. E. Mitscherlich showed that red, monoclinic selenium is completely soluble in carbon disulphide, forming a red soln. M. Coste said that metallic selenium is slightly soluble in carbon disulphide, but A. P. Saunders found that it is completely insoluble in that solvent; observations to the contrary indicated that the selenium had not been all transformed into the metallic variety. E. Petersen found that the highest degree of purity he could prepare still contained about one per cent. of soluble selenium. R. Marc gave for the solubility of his *A*-metallic selenium 3·4 parts per 100 parts of solvent, and after being kept for 2 days at 190°–200°, 2·0 parts of the resulting *B*-form dissolved in 100 parts of boiling solvent. W. E. Ringer found that selenium dissolves in carbon disulphide only to the extent of one part per 1000, but with sulphur-selenium mixtures selenium can be dissolved up to the extent of one part per 100. B. Rathke found that **carbon diselenide** dissolves vitreous selenium, and so does **ethyl sulphide** and **ethyl selenide,** but the metallic selenium is insoluble in ethyl sulphide, and in **carbon tetrachloride.** According to C. Chabrié, selenium reacts with **zinc ethide,** forming the selenium analogue of zinc mercaptan. J. W. Retgers found that 100 parts of **methylene iodide** dissolve 1·3 parts of vitreous or of metallic selenium at 12°. M. Coste found that metallic selenium is slightly soluble in **toluene, nitrobenzene, quinoline,** and **aniline;** A. P. Saunders observed its solubility in hot quinoline, **ethyl benzonate,** aniline and **naphthalene;** and, added E. Beckmann and W. Gabel, quinoline reacts with selenium giving off hydrogen. C. Chabrié observed no reaction between **benzene** and selenium in the presence of aluminium chloride. As indicated in connection with the allotropic forms of selenium, vitreous selenium dissolves in benzene, **isobutyric acid, acetophenone, acetone, chloroform, thiophene, toluene, benzonitrile, ethyl acetate,** and **alcohol,** forming red crystals; and in quinoline, aniline, **pyridine,** etc., forming metallic selenium. E. C. Franklin and C. A. Kraus found that selenium dissolves in a soln. of **potassium cyanide,** forming potassium selenocyanate. I. Williams studied the action of selenium on **rubber.** J. Dean, and H. Stolte studied some organic compounds of selenium. A. Mailhe and M. Murat, K. van der Grinten, A. Cousen and W. E. S. Turner, S. Sugie, and H. Wayts and G. Gosyns studied the action of selenium on organic magnesium compounds; and K. W. Rosenmund and H. Harms, on bromobenzoic acid. F. W. Bergstrom found that selenium in liquid ammonia soln. readily reacts with the **cyanides** of many metals, forming selenocyanides.

The coloration of **glass** with selenium has been discussed by F. Kraze, P. Fenaroli, K. Fuwa, K. van der Grinten, and E. Zschimmer. P. Fenaroli attributed the colour produced by sulphur to the presence of polysulphides, but in consequence of the more pronounced electro-positive character of selenium and tellurium, these elements have less tendency to form corresponding polyselenides and polytellurides, and glasses may readily be obtained in which the colour is due to elementary selenium or tellurium in colloidal form. The range of colour in presence of these elements is very much greater than in glasses coloured by sulphur, and the variations of colour are attributable to variations in the degree of dispersity of the selenium and tellurium. Glasses which contain dispersed selenium in the form of polyselenides have a chestnut-brown colour; those which contain colloidal selenium vary from yellow to reddish-violet. The action of selenium on the **metals** is discussed in connection with the respective selenides—*vide* also hydrogen selenide for the action of mercury and its vapour. F. W. Bergstrom found that selenium in liquid ammonia soln. slowly attacks copper, magnesium, and zinc. P. Guyot said that a soln. of selenium in carbon disulphide precipitates a certain number of the metals from alkaline soln. as selenides, but, excepting silver salts, it does not precipitate acid or neutral salt soln. F. Garelli and A. Angeletti could not confirm this statement. G. Calcagni found that powdered selenium dissolves readily in a cold soln. of 66 per cent. **sodium or potassium hydroxide.** The reactions which occur are complex. Selenides are first formed, and these pass into polyselenides and selenites. Possibly a compound analogous to thiosulphate is produced by the action of atm. oxygen on the selenides, and a small part of the selenium may be present as such in the soln. The brown soln. are gradually decolorized by oxygen and carbon dioxide from the air. M. Coste also found metallic selenium dissolves in potash-lye. R. D. Hall and V. Lenher found that selenium is not an active reducing agent; it reduces soln. of **gold salts** only when boiled; and with **silver salts,** silver selenide is formed which acts as a reducing agent towards gold chloride soln. P. Senderens found that powdered selenium acts more readily than sulphur on a boiling aq. soln. of silver nitrate, for the reduction with selenium is almost complete; the precipitation of the silver by tellurium is always complete, and if the tellurium is in excess, the nitric acid which is formed is decomposed with production of nitrogen peroxide even in dil. soln. Silver nitrate in soln. is completely, although slowly, reduced by selenium and tellurium at the ordinary temp.; **cupric nitrate** is not affected under the same conditions, but is partially reduced by tellurium on heating. F. Garelli and A. Angeletti said that the silver may be precipitated completely if an excess of selenium be employed, and the soln. be boiled. From a neutral soln. containing silver, lead, and mercurous or mercuric nitrate, the silver may be precipitated completely in this way, the amount of selenium added being boiled for fifteen minutes and filtered when cold. The precipitate is heated with nitric acid and the silver estimated as chloride. A. Gutbier and co-workers, and E. Kessler studied the purple-coloured substance produced by the deposition of selenium on **stannic hydroxide,** analogous to purple of Cassius—*selenium-tin purple.* H. Lessheim and co-workers discussed the co-ordination number of selenium in its complex salts.

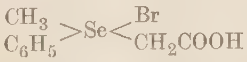
Some reactions of analytical interest.—Selenium forms selenious and selenic acids; the former is produced by the action of nitric acid on selenium, or by dissolving the dioxide in water, and the latter, by fusing selenium with a mixture of alkali carbonate and nitrate, and treating the resulting alkali selenate with acid. With **hydrochloric acid,** selenic acid behaves like a peroxide giving off chlorine when boiled, and is at the same time reduced to selenious acid: $H_2SeO_4+2HCl=H_2O+Cl_2+H_2SeO_3$. Selenious acid or an alkali selenite, in aq. soln. or in dil. hydrochloric acid soln., when treated with **hydrogen sulphide,** gives a lemon-yellow precipitate of selenium and sulphur: $H_2SeO_3+2H_2S=3H_2O+Se+2S$, and the precipitate is soluble in ammonium sulphide. Hydrogen sulphide does not give a precipitate with selenic acid, unless the soln. be boiled with hydrochloric acid so as to reduce the selenic to selenious acid. Selenic acid is not reduced by **sulphur dioxide,** but this agent, as well as other reducing agents, gives a red or black precipitate of selenium with a soln. of selenious acid in dil. hydrochloric acid. The reaction was examined by E. Keller,[2] C. Alexi, etc. A. Jouve said that one part of selenium in 10,000 parts of soln. can be detected by this means. H. Rose regarded the presence of hydrochloric acid as an essential factor in the complete reduction of selenium salts—*vide* Figs. 1 and 2. H. Rose, C. Alexi, and A. Gutbier found the reduction is effected by **phosphorous acid;** A. Gutbier and E. Rohn, **hypophosphorous acid;** J. Meyer and J. Jannek, **sodium hyposulphite,** which enables one part of selenium in 20,000 parts of soln. to be detected; A. Grak and J. Pretén, **stannous chloride;** E. Keller, **ferrous sulphate;** A. Jouve, **acetylene,** which enables one part of selenium in 100,000 parts of soln. to be detected; F. Stolba, **glucose;** L. Kastner, **magnesium** or **aluminium;** H. Reinsch, copper; A. W. Pierce, F. A. Gooch and W. G. Reynolds, C. Alexi, and W. Muthmann and J. Schäfer, **potassium iodide** and hydrochloric acid—J. F. Norris and H. Fay, and P. Klason and H. Mellquist based a volumetric process on this reaction; J. Meyer and W. von Garn detected 0·002 per cent. of selenium dioxide by its means; and P. Jannasch and M. Müller, C. Alexi, G. Pellini and co-workers, J. Jannek, and A. Gutbier and co-workers, **hydrazine salts,** and **hydroxylamine salts.** Neutral soln. of selenites give a white precipitate with **barium chloride,** which is soluble in dil. acids; with selenates, a white precipitate insoluble in dil. acids is formed, and it dissolves with the evolution of chlorine when boiled with hydrochloric acid. A. Hilger and E. von Gerichten found that selenious acid gives with **magnesia**

mixture a colourless precipitate of magnesium selenite insoluble in acids. With selenious acid, **copper sulphate** soln. gives a greenish-blue precipitate, but no precipitation occurs with selenic acid. G. Denigês found that soln. of selenic acid or selenates mixed with a soln. of 10 grms. of **mercurous nitrate,** 10 c.c. of nitric acid of sp. gr. 1·39, and 100 c.c. of water, give a crystalline precipitate, and selenious acid and selenites give a precipitate with needle-like crystals. E. Schmidt detected 0·0005 per cent. of selenious acid in sulphuric acid by adding 0·01 grm. of **codeine phosphate** to 10 c.c. of soln., when a distinct green colour is produced in a minute and a bluish-green coloration in 15 minutes of selenious acid is present. When the dilution of the selenious acid is as low as 0·0001 per cent. the colour reactions can be observed with sufficient sharpness against a white surface, and in comparison with a soln. of about 0·01 grm. of codeine phosphate in 10 c.c. of pure sulphuric acid. The process is not applicable when the sulphuric acid contains iron (for example, 1 drop of ferric chloride in 10 c.c. of sulphuric acid), but it is not influenced by sulphurous acid, and is only retarded, not vitiated, by the presence of tellurous acid. A sulphuric acid soln. of **indigo** is decolorized by selenic acid. When selenium or one of its compounds is melted with **potassium cyanide** in a stream of hydrogen, potassium selenocyanide is formed which does not precipitate selenium when exposed to air, but does when boiled with hydrochloric acid. A. C. Vournasos[3] obtained selenium hydride by heating selenium with **sodium formate** to 400°. For the biological test, *vide infra*. The effect of selenium on the tests for arsenic was discussed by O. Rosenheim.

The physiological action of selenium.—The peculiar smell of burning selenium was attributed by J. J. Berzelius to the formation of selenium monoxide; and by F. Sacc, and V. Lenher to the presence of traces of moisture, forming hydrogen selenide. According to B. Rathke, the characteristic radish-like odour of selenium when heated on charcoal before the blowpipe is due to carbon diselenide and not to a selenium suboxide. F. Czapek and J. Weil found that the element selenium is not poisonous. I. O. Woodruff and W. J. Gies said that when the element is taken in by the mouth, it is discharged *per rectum* and does no harm. F. Czapek and J. Weil could not demonstrate any direct toxic action of selenium compounds on cells, but they act poisonously on the animal body as a whole, and selenites more so than selenates. F. Riechen described a fatal case of poisoning by sodium selenite in coffee. The symptons resembled those of arsenical poisoning. P. C. Chabrié and L. Lapicque, F. Czapek and J. Weil, C. O. Jones, I. O. Woodruff and W. J. Gies, and F. Lehmann were unable to demonstrate any direct toxic action of selenium on the cells of the animal organism, but concluded that selenium compounds act poisonously on the animal body as a whole. The poisonous nature of the selenium compounds was placed beyond doubt by F. W. Tunnicliffe and O. Rosenheim. F. Czapek and J. Weil suggested that the selenates are reduced to selenites in the body. The effect of selenium is likened to that of arsenic and antimony, for it acts by weakening the heart, lowering the blood pressure, and paralyzing the central nervous system. I. O. Woodruff and W. J. Gies also emphasized the analogy of the effects produced by selenium and arsenic. Four mgrms. of the selenite or selenate per kgrm. of body weight in dogs, kill in a few minutes. The introduction of soluble salts is quickly followed by its elimination in the breath, and urine. C. O. Jones added that in the body, selenate is reduced to selenite; a small quantity is excreted in the urine, and the remainder is carried to the spleen and liver, where it is reduced by dextrose to selenium; when dextrose furnished from the glycogen is becoming exhausted, fat is called on. There is a retention of chlorides, a disappearance of hydrochloric acid, and a great relish for sodium chloride. This is interpreted as meaning that the salt raises the sugar in the blood to satisfy the selenite, and so protect the cells from toxic effects. Sodium selenite does not produce hæmolysis outside the body, but does so after hypodermic injection; it is reduced to selenium in the portal circulation, chiefly in the spleen and liver. Only a proportion of the red corpuscles are hæmolyzed, suggesting that those from the portal system were mixed in the general circulation with those which are unaffected. Glycogen and sugar disappear in a remarkable manner after the injection. A. H. Roffo and S. M. Neuschloss found that selenium compounds augment the separation of normal cells in adult white rats, and diminish that of normal cells of new-born animals, embryos, and of carriers of neoplasms.

B. Gosio observed that selenites are attacked by micro-organisms, forming a red substance, probably selenium. The subject was discussed by G. Joachimoglu and co-workers. In addition to the *Thiobacillus thioxidans*, J. G. Lipman and S. A. Waksman observed that other bacteria can derive their energy from the oxidation of selenium to selenic acid. F. Lehmann found that a high conc. of selenium is lethal to trypanosomes, but after one hour's exposure, the conc. 1 : 5000 for selenites and 1 : 100 for selenates is not lethal. A. Nemec and V. Kas found that sodium selenate exerts a favourable influence on the growth of dry mycelium in the *Penicillium roqueforti* connected with the cheese industry, but with the *Penicillium candidum* a toxic effect occurs when the selenate is increased beyond a certain limiting conc. E. Keyssner was unable to prove that selenium exerts any curative effect on cancer. The effect on plants was studied by A. Nemec and V. Kas, and B. Turina ; and as a weed-killer, as well as a fungicide or a bactericide for plant diseases by F. M. Lougee and B. S. Hopkins, and N. M. Stover and B. S. Hopkins. According to A. Maassen and co-workers, in the living organism, the selenates are reduced to selenites and selenium, and in the case of animals, the selenium is converted into selenium ethide, and in the case of bacteria, into selenium methide. O. Rosenheim found that the so-called biological test for arsenic (*q.v.*) is applicable also to selenium compounds which are decomposed by *Penicillium brevicaule* giving a very disagreeable odour resembling to some extent skatol or mercaptan. The test is very sensitive, 0·01 mgrm. of selenium in 1 c.c. of liquid is easily demonstrated by a vigorous growth of the mould. Elemental selenium, unlike arsenic, is not attacked by the mould. J. Stoklasa found that both selenites and selenates exert a markedly injurious action on the germination of seeds. Selenates are much less toxic than selenites, and at a great dilution even exert a favourable influence. Thus, sodium selenate at a conc. of 5×10^{-6} up to 10^{-5} gram-atoms of selenium per litre produces a stimulating effect on the growth of maize, but at higher conc. it is toxic. B. Turina inferred that selenium does not enter the mature plant system in appreciable quantities by way of the root-hairs, but that the root-cap plays the important *rôle* of point of entry and filtration.

The atomic weight and valency of selenium.—Selenium resembles sulphur very closely in its typical compounds. It may be bi-, quadri-, or sexivalent. It is bivalent in gaseous hydrogen selenide, H_2S, and in organic and inorganic selenides typified by $(CH_3)_2Se$, and K_2Se ; and $Se(C_2H_5)_2$ measured by Y. Tanaka and Y. Nagai. It is quadrivalent in a number of *selenomium* compounds—*e.g.* $(C_2H_5)_3SeI$, and $(C_2H_5)_3Se(OH)$, prepared by L. Pieverling ;[4] in $(CH_3)_2Cl_2$, and $(C_6H_5.CH_2)_2SeCl_2$, prepared by C. L. Jackson ; in $(C_2H_5)_2SeCl_2$, and $(C_2H_5)_3SeCl$, prepared by B. Rathke ; in $(CH_2COCH_3)_2SeCl_2$, and $(CH_2COC_4H_5)_2SeCl_2$, prepared by A. Michaelis and F. Kunckell ; in selenium dioxide, SeO_2, and in selenious acid, $SeO(OH)_2$ which, unlike sulphurous acid, is a true dihydrozyl-compound showing no signs of tautomerism ; and it is also quadrivalent in $SeO(OC_2H_5)$ obtained by A. Michaelis and B. Landmann. Selenium is sexivalent in the gaseous hexafluoride, SeF_6, prepared by E. B. R. Prideaux, and probably also in selenic acid, H_2SeO_4, and in the selenates which are isomorphous with the sulphates. W. J. Pope and A. Neville prepared optically active selenium compounds, *e.g.*



$$\begin{matrix}CH_3\\C_6H_5\end{matrix}>Se<\begin{matrix}Br\\CH_2COOH\end{matrix}$$

discussed by M. Scholtz, R. F. Goldstein, W. J. R. Henley and S. Sugden, etc. M. Padoa, W. R. Gaythwaite and co-workers, O. R. Edwards and co-workers, and

G. T. Morgan and F. H. Burstall, discussed the valency of selenium. According to T. M. Lowry, the arguments with respect to the tetrahedral configuration of sulphur compounds apply also to selenium.

The atomic weight of selenium was first determined by J. J. Berzelius[5] by sat. 100 parts of selenium with chlorine. He found that this gave 179 parts of chloride. Hence, with chlorine 35·4584, Se : 4Cl=100 : 179, the at. wt. of selenium is 79·24. J. B. A. Dumas also used this method, and from his results obtained the ratio 100 : 178. The values with selenium tetrachloride are rather high, presumably because of a slight contamination with selenium oxychloride. E. Mitscherlich analyzed some alkali selenates, but the results are not suitable for computing the at. wt. F. Sacc tried reducing barium selenite and weighing the resulting barium sulphate and selenium, but obtained discordant results; and similarly also with lead and silver selenites. He obtained better results by converting barium selenite into the sulphate, and from the ratio $BaSeO_3 : BaSO_4 = 100 : 88{\cdot}437$ obtained the at. wt. 78·587 (Ba, 137·363). F. Sacc converted selenium into the dioxide by means of nitric acid, but obtained poor results. J. Meyer obtained better results by converting selenium into the dioxide in a current of nitrogen peroxide and oxygen at 215°, and he obtained 79·135 for the at. wt. from the ratio $Se : SeO_2$, and J. Jannek and J. Meyer obtained 79·141 by this process. J. Meyer also reduced the dioxide to selenium as a control, and F. Sacc reduced the dioxide to selenium with ammonium hydrosulphite, and obtained a ratio $SeO_2 : Se = 100 : 71{\cdot}080$; there follows the at. wt. 78·6. A. Schrötter similarly obtained 78·6: and G. Ekman and O. Pettersson, 79·08. O. L. Erdmann and R. F. Marchand analyzed mercuric selenide, and from the ratio $HgSe : Hg = 100 : 71{\cdot}7327$ there follows the at. wt. 78·883. G. Ekman and O. Pettersson also ignited silver selenite, and from the ratio $Ag_2SeO_3 : 2Ag = 100 : 62{\cdot}9002$ there follows for the at. wt. 79·259. The silver was probably contaminated with traces of selenium. V. Lenher transformed silver selenite into the chloride, and from the ratio $Ag_2SeO_3 : 2AgCl = 110 : 83{\cdot}558$, there follows the at. wt. 79·328. He also reduced silver bromoselenate to selenium by means of hydroxylamine hydrochloride, and obtained the ratio $(NH_4)_2SeBr : Se = 100 : 13{\cdot}3224$, which furnishes the at. wt. 79·248. O. Steiner analyzed phenylselenide, and from the ratio $(C_6H_5)_2Se : 12CO_2 = 100 : 226{\cdot}536$, there follows the at. wt. 78·97. J. Meyer electrolyzed a soln. of silver selenite in one of potassium cyanide, and obtained 62·9193 per cent. of silver which yields the at. wt. 79·155. P. Bruylants and A. Bytebier calculated from the density and compressibility of hydrogen selenide the at. wt. 79·18; later determinations by P. Bruylants and J. Dondeyne gave 79·37, and by P. Bruylants and co-workers, 79·23. F. W. Clarke calculated for the best representative value 79·176; and the International Table for 1926 gives 79·2.

The **atomic number** of selenium is 34. F. W. Aston[6] found that selenium consists of six **isotopes** with at. wts. respectively 82, 80, 78, 77, 76, and 74. E. Rutherford and J. Chadwick, and H. Müller observed no evidence of **atomic disintegration** when selenium is bombarded by α-rays, but H. Pettersson and G. Kirsch observed some evidence of atomic disruption. The subject was discussed by G. I. Pokrowsky. A. L. Foley studied the action of ultra-violet light, and of X-rays on selenium confined in sealed glass tubes when the spectra are periodically examined. The results were indefinite. N. Bohr represented the **electronic structure** (2) (4, 4) (6, 6, 6) (4, 2). The subject was discussed by M. L. Huggins, W. Kistiakowsky, C. P. Smyth, H. Collins, H. G. Grimm and A. Sommerfeld, S. Meyer, and C. D. Niven.

The uses of selenium.—Selenium is used in preparing a scarlet-red colour for glass, glazes, and enamels.[7] S. C. Lind[8] described diethyl selenide as an anti-knock agent for petrol. A. D. Little, and E. G. Crocker discussed the use of selenium in the production of flame-proof, insulated, electric wires, paper, etc. C. Dickens used colloidal selenium as a germicide, insecticide, fungicide, and for preservation of wood; and F. M. Lougee and B. S. Hopkins recommended using selenium compounds in place of sulphides. There are some applications based on its remarkable sensitiveness to light whereby light can be converted into electrical energy. In conjunction with a relay, the selenium cell can be employed for starting and stopping a motor, ringing a bell, lighting lamps, firing cannons, etc., at a distance. Selenium cells have been used in the protection of safes, so that they give an alarm when exposed to the light from a burglar's lantern. They have been used for the lighting of buoys using compressed gas. When the sun rises in the morning, the resistance of the cell is lowered, and this operates a switch which causes the gas to be turned off; as night approaches, the resistance of the cell increases and the gas is turned on again. The light of a distant lighthouse or railway signal can be focussed upon the cell and so indicate either the lighting up or extinction of lamps. Attempts have been made to steer aerial torpedo boats automatically from the ground and so attack, say Zeppelin air-ships in mid-air. The selenium cell has been employed in the construction of photometers whose readings are not vitiated by the personal error characteristic of ordinary photometers. The selenium cell has been used in stellar photometry; and in the study of the solar eclipse. Efforts have also been directed towards the employment of the selenium cell for discriminating differences of colour, but not yet successfully, although there is a patent for a contrivance for sorting coloured objects, like cigars or unroasted coffee beans, automatically by the colour. The selenium cell has been employed in the transmission of speech over 15 miles. The photogramophone is an arrangement for the reproduction of speech, and music. Words spoken into the transmitter superpose the current variations in the telephone circuit on the current flowing in the arc-light and cause a corresponding variation in the light. When the developed film is arranged so that the rays from an arc-light pass through the film and intermittently impinge on a selenium cell, the variations in the resistance of the cell connected with a telephone receiver reproduce the sounds originally spoken into the transmitter. This is a talking kinematographic film. The selenium cell has also been applied to the transmission of photographs over existing telephone or telegraph wires—telephotography, picture telegraphy, and in television. There are instruments also for converting light into sound through the medium of an electric current, and applied—optophone, phonoptikon, photophone, etc.—so as to enable the blind to read printed books, newspapers, typewritten documents, etc.

The varied applications are discussed in special works—C. Ries, *Das Selen*, München, 1918; E. E. Fournier d'Albe, *The Moon Element*, London, 1914; E. Ruhmer, *Das Selen und seine Bedeutung für die Elektrotechnik*, Berlin, 1902; L. Ancel, *Scient. Amer. Monthly*, **1**. 28, 157, 253, 1920; *Chim. Ind.*, **2**. 73, 245, 1919; W. Späth, *Naturwiss.*, **10**. 14, 1922; H. Thirring, *Zeit. tech. Phys.*, **3**. 118, 1922; V. Lenher, *Journ. Ind. Eng. Chem.*, **12**. 597, 1920; *Trans. Amer. Inst. Min. Met. Eng.*, **69**. 1035, 1923; Anon., *Chem. Trade Journ.*, **76**. 635, 1925; E. E. F. d'Albe, *Scient. Amer. Suppl.*, **83**. 307, 1917; M. F. Doty has compiled *Selenium—A List of References, 1817–1915*, New York, 1927.

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§ 6. Hydrogen Selenides

J. J. Berzelius[1] discovered **hydrogen selenide,** H_2Se, in 1817, in his study of the action of hydrochloric acid on potassium and ferrous selenides. It can be obtained by the direct union of the elements. P. Hautefeuille prepared the gas by heating selenium and hydrogen in a sealed tube at 440° ; F. Jones, by heating selenium and hydrogen at ordinary atm. press.; and B. Corenwinder, by passing a mixture of hydrogen and selenium vapour over pumice-stone at 440°. M. G. Weber obtained the best yield with the pumice-stone at 350°. The yields were 43·7 per cent. at 300°; 48·2 per cent. at 325°; 58·0 per cent. at 350°; 53·8 per cent. at 375°; 50·7 per cent. at 400°; and 44·0 per cent. at 450°. To purify the gas, it was first passed through a cooling tube to condense the selenium vapour and then condensed to a solid by cooling in liquid air, and fractionally sublimed. W. Hempel and M. G. Weber recommended this mode of preparation. P. Bruylants and A. Bytebier said that the gas, dried by phosphorus pentoxide, can be condensed in a freezing mixture of solid carbon dioxide and ether, and purified by distillation and sublimation. J. J. Berzelius collected the gas over mercury, and P. Bruylants and A. Bytebier added that if moisture be excluded the gas does not attack mercury. F. Wöhler and H. Uelsmann prepared the gas by passing a slow current of hydrogen over selenium heated to the temp. at which it vaporizes; and R. Januario added that the union does not occur at 350°, and the hydrogen selenide can be detected only when the selenium is near its b.p. This is not quite right, for A. Ditte, and H. Pélabon observed that the union of the two elements occurs in the neighbourhood of 250°; that the speed of the reaction increases proportionally with a rise of temp. up to about 500° when the proportion of hydrogen selenide which is formed attains a maximum, for there is a decrease in the proportion formed as the temp. rises beyond this value. Thus, the proportion of hydrogen selenide formed from its elements was found to be:

	203°	250°	305°	350°	440°	500°	520°	590°	640°
H_2Se . .	0	6·8	22·4	37·8	51·7	60·7	63·9	47·3	43·1

and the presence of porous substances facilitate the reaction. He also showed that the reaction $H_2+Se=H_2Se$ is reversible for hydrogen selenide, even at 150° suffers a slight decomposition; the proportion dissociated increases towards 270° and then decreases as the temp. rises until a minimum is reached at about 500°. Beyond that temp., the proportion dissociated increases as the temp. rises. Thus:

	155°	203°	250°	272·5°	305°	325°	350°	440°
H_2Se . .	37·0	27·7	24·6	20·2	22·6	28·9	37·9	51·7

H. Pélabon showed that the results observed by A. Ditte are affected to some extent by the absorption of hydrogen selenide by the liquid selenium. He said that the maximum proportion of hydrogen selenide formed is about 41 per cent. at 575°. He therefore worked with the smallest excess of selenium, and obtained the results summarized in Fig. 32. For the fractional part of hydrogen selenide in the gas, that is, the ratio of the partial press. of the hydrogen selenide, p_2, to the total press. of the hydrogen, p_1, and the hydrogen selenide, H. Pélabon found for the formation of hydrogen selenide (curve *BC*, Fig. 32):

	350°	380°	440°	470°	480°	500°	608°	620°	660°	705°
$P_2/(p_1+p_2)$.	28·40	28·30	35·16	37·5	38·12	39·20	41·10	39·85	39·1	3·800

For the thermal decomposition of hydrogen selenide (curve *BC*, Fig. 32):

	350°	440°	480°	660°
$p_2/(p_1+p_2)$ . .	22·50	34·69	40·73	39·60

The ratio of the partial press. of the hydrogen, p_1, to that of the hydrogen selenide, p_2, can be represented by $\log (p_1/p_2)=13170\cdot3T^{-1}+15\cdot53 \log T+119\cdot88$, where T denotes the absolute temp., and this agrees with the observed results. It follows from this that the ratio $p/(p_1+p_2)$ is a maximum when the temp. is 575°, a result confirmed by observation. The maximum at 575° indicates that the heat of formation of hydrogen selenide is zero at this temp.—*vide* **2**. 18, 4. The calculated value −17·38 Cals. is in agreement with C. Fabre's value −18·0 Cals. at 15°. Above 575° the heat of formation should be positive and below that temp. negative. The lowest limit at which any direct formation of hydrogen selenide can be observed is

250° (*E*, Fig. 32); and at 270°, the ratio $p_2/(p_1+p_2)$ is nearly 0·048, whether the system be heated for 490 hrs. or a month. When hydrogen selenide is kept for 192 hrs. or 490 hrs. at 270°, this ratio is near 0·16, whereas the equation for log (p_1/p_2) requires the value 0·10. At still lower temp., the curve *DB*, Fig. 32, is produced. In agreement with P. Duhem, H. Pélabon assumes that the above equation represents *la ligne des équilibres véritable*—*ABC*, Fig. 32; while the curve *DB* separates the region in which hydrogen selenide decomposes from *la région des faux équilibres;* where hydrogen selenide is neither decomposed nor formed directly from its elements, and the curve *EB* separates the region in which hydrogen selenide is formed from its elements from the region of false equilibrium. M. Bodenstein denied H. Pélabon's conclusion that true equilibrium in the reaction $H_2+Se=H_2Se$ occurs only above 350°, and that both the formation and decomposition of hydrogen selenide comes to a standstill short of the point of equilibrium. M. Bodenstein found that the reaction is catalyzed by the deposit of selenium in the containing vessel, and that the decomposition of the selenide proceeds slowly until selenium is deposited when the speed is much accelerated. The progress of the reaction follows the mass law $dx/dt=k(a-x)-k_1x$, when a denotes the initial conc. of the hydrogen; or, if ξ denotes the maximum value of x at the point of equilibrium, and the initial conc. of hydrogen unity, $k=(\xi/t)\log\xi/(\xi-x)$. With half the bulb coated with selenium, $k=0{\cdot}000119$, when completely coated, $k=0{\cdot}000251$; and an increase of surface relatively to the vol. raises k to 0·000527. This shows that the process is mainly a wall-reaction. True equilibrium is attained even below 320°, thus:

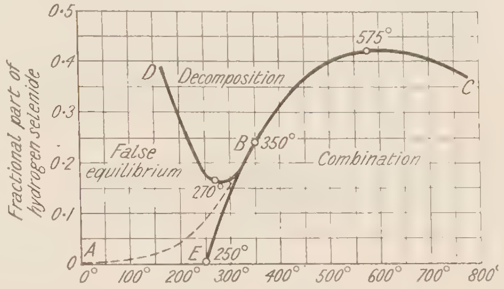

FIG. 32.—Effect of Temperature on the Formation and Decomposition of Hydrogen Selenide.

	254°	274°	301°
ξ Formation	0·1388	0·1692	0·2052
ξ Decomposition	0·1391	0·1701	0·2046

M. Bodenstein could not confirm H. Pélabon's minimum dissociation at 570°—*vide supra*, hydrogen sulphide. H. Pélabon examined the influence of *pressure* on the union of hydrogen and selenium in sealed tubes. The ratios $p_2/(p_2+p_2)$ at 620° for press. 520 mm., 1270 mm., 1520 mm., and 30,160 mm. were respectively 0·405, 0·402, 0·42, and 0·423. At 575° for press. of 678 mm. and 1380 mm., the ratios were 0·39 and 0·403 respectively. At a much lower temp., namely, 310°, and press. of 580 mm. and 1520 mm., the ratios were 0·214 and 0·23 respectively. It follows, in agreement with the ordinary theory of dissociation, that, as A. Ditte has already observed, an increase of press. increases very slightly the quantity of hydrogen selenide produced at a given temp., and the effect of press. is less the higher the temp. An increase of press. increases the rate of formation of the hydrogen selenide. N. N. Beketoff and N. A. Czernay found that 47 per cent. of hydrogen selenide is dissociated at 440°, and that in the series H_2O, H_2S, and H_2Se, the percentage dissociation at any temp. is greater the larger the mol. wt. of the compound.

A. Pleischl said that when moist selenium is sublimed, some hydrogen selenide is formed. E. Trautmann said that reducing agents transform selenium into hydrogen selenide; and P. Hautefeuille observed that red or black selenium is transformed by hydrogen iodide into hydrogen selenide; the former process requires 2·14 Cals. per eq. (*i.e.* 40·7 grms.) of hydrogen selenide, and the latter, 2·70 Cals. If conc. hydriodic acid and selenium be heated in a sealed tube, hydrogen selenide is formed, but as the vessel cools, hydriodic acid and crystalline selenium are produced. J. J. Berzelius obtained hydrogen selenide when selenium dissolves in acids. M. E. Pozzi-Escot found that hydrogen selenide is formed by the action of the hydrogenases—*e.g.* philothion—on selenium. A. Étard and H. Moissan prepared hydrogen selenide by heating selenium with a hydrocarbon—*e.g.* colophene—because its b.p., 300, is above the m.p. of selenium. The reaction takes place in two stages—first, a substitution product is formed, and this is subsequently decomposed. Only a mixture of carbon and unaltered colophene is left at the end of the operation. M. G. Weber said that the yield is poor; the gas produced contained 30·8 per cent. of hydrogen selenide along with 10·7 per cent. of nitrogen; 6·6 of hydrogen; 13·6 of methane; 24·1 of carbon monoxide; 6·5 of carbon dioxide; 0·7 of oxygen; and 7·0 per cent. of other hydrocarbon gases. H. Wuyts and A. Stewart used paraffin wax at 335°–340°. A. C. Vournasos found that when a mixture of selenium and sodium formate is heated to 400°, selenium hydride is formed in limited yield owing to decomposition of the gas.

J. J. Berzelius found that when potassium or ferrous selenide is warmed with hydrochloric acid, hydrogen selenide is given off, and it can be collected over mercury. E. Divers and T. Shimidzu said:

> In preparing the hydrogen selenide required we imitated the common process of preparing hydrogen sulphide. An iron selenide was first made by projecting into a black-lead pot, heated in a wind-furnace, a mixture of wrought-iron filings and selenium. In this operation most of the selenium was dissipated in vapour. When the iron had grown hot more selenium was added which combined with the iron with very little loss, causing vivid ignition and complete liquefaction of the whole. The fluid compound was run into a mould and cooled. The solid mass thus obtained was indistinguishable in appearance from iron sulphide similarly prepared. Not being very sensitive to the action of acids, it was powdered before being put in the apparatus for generating the gas, and then warmed with dil. hydrochloric acid. This gave a steady stream of gas.

M. G. Weber obtained better yields of hydrogen selenide by this process than by any of the others tried; but only about half the selenium employed in preparing the iron selenide is recovered as hydrogen selenide because some of it is consumed in the formation of selenium-iron compounds which do not give hydrogen selenide with acids. H. Fonzes-Diacon obtained hydrogen selenide by the action of water on aluminium selenide; P. Bruylants and co-workers found the product is of a high degree of purity. R. de Forcrand and H. Fonzes-Diacon recommended this process, using water previously boiled to ensure the absence of air, and keeping the aluminium selenide in excess; P. Bruylants and A. Bytebier also said that this is the most satisfactory way of preparing the gas; and L. Moser and E. Doctor slowly dropped the selenide—magnesium or aluminium for preference into dil. acid. A. Burger and M. W. Neufeld employed an apparatus for preparing the gas on the plan of the hydrogen sulphide generators. H. Hahn, and B. Rathke obtained hydrogen selenide by the action of water or steam on phosphorus pentaselenide, or, according to W. Bogen, by the action of alcohol on the pentaselenide. W. Becker and J. Meyer obtained the pentaselenide by intimately mixing and heating 11 grms. of phosphorus and 66 grms. of selenium, and when this is mixed with water and warmed a little a stream of the gas is given off. If alcohol or a mixture of alcohol and water is employed, the current of gas is feebler. M. G. Weber found that the yield is poor. L. Moser and E. Doctor prepared the gas by dropping aluminium or magnesium selenide slowly into a dil. acid. F. Ephraim and E. Majler found that when the selenophosphates are dissolved in water, particularly warm water, they are decomposed with the evolution of hydrogen selenide: $M_3PSe_4+4H_2O=M_3PO_4+4H_2Se$. M. G. Weber said that the yield of gas is poor, and the selenophosphates are not often available. M. G. Weber tried to make hydrogen selenide by the electrolysis of 50 per cent. sulphuric acid using a selenium cathode, as in the case of hydrogen telluride, but he observed only a disintegration of the selenium; no hydrogen or hydrogen selenide was formed.

J. J. Berzelius described hydrogen selenide as a colourless gas which smells something like hydrogen sulphide, but subsequently produces dryness and a pungent, astringent, and painful sensation in all parts of the mucous membrane of the nose with which the gas has come in contact; a bubble of the gas no larger than a pea produces inflammation of the eyes; destroys the sense of smell for several hours; and frequently brings on a cold in the head or a dry, painful cough which lasts a fortnight. R. de Forcrand and H. Fonzes-Diacon said that hydrogen selenide is more toxic than the sulphide or telluride. P. Bruylants and A. Bytebier found that the **weight of a litre** of hydrogen selenide under normal conditions is 3·6715 grms., and later, P. Bruylants and co-workers gave 3·6624 grms. as the mean of 53 determinations. At 1, 0·6, and 0·3 atm. press., respectively, P. Bruylants and J. Dondeyne found 3·6721, 3·65732, and 3·6440 grms. for the wt. of a normal litre. R. de Forcrand and H. Fonzes-Diacon gave 2·12 for the **specific gravity** of the liquid at its b.p. (—42°), and for the **molecular volume** of the liquid, 38·11. E. Rabinowitsch gave 38·3 for the mol. vol. H. Remy discussed the structure of hydrogen selenide. P. Bruylants and P. Dondeyne found for $p=1·0000$, $pv=1·0000$; for $p=0·60000$; $pv=1·00404$; and for $p=0·3$, $pv=1·00769$; for the coeff. of **compressibility,** 0·0000573; and for the deviation from Boyle's law, $A=1-p_cv_c/pv$, between 0 and 1 atm., $A_0{}^1=0·1083$ when calculated by Guye's method—**1.** 5, 8—and 0·1302 when calculated from direct measurements of pv. K. Olschewsky found that the gas at 0° liquefies under a press. of 6·6 atm.; at 18°, 8·6 atm.; at 52°, 21·5 atm.; at 100°, 47·1 atm.; and at the critical temp., 137°, 91·0 atm. C. J. Smith found the **viscosity** of the gas at 20° to be 0·000168, and he calculated Sutherland's constant to be 365. The **mean collision area** of the mol. is $0·96\times10^{15}$ sq. cm. He also made some speculations on the electronic structure of the molecule. K. Olschewsky also found that at —68°, the liquid freezes to a solid, which, according to R. de Forcrand and H. Fonzes-Diacon, has a **melting point** of —64°. They also gave for the **vapour pressure** at —42°, one atm.; at —30°, 1·75 atm.; at 0·2°, 4·5 atm.; and at 30·8°, 12 atm. P. Bruylants and J. Dondeyne gave for the vap. press., p mm.:

	−78·01°	−65·90°	−54·76°	−44·35°	−41·26°	−35·98°	−25·56°	−26·77°
p .	82·89	203·33	400·55	654·51	760·83	942·41	1464·06	1799·0

K. Olschewsky gave —41° for the **boiling point** at 760 mm.; P. Bruylants and J. Dondeyne, —41·2°; and R. de Forcrand and H. Fonzes-Diacon, —42°. The **critical temperature** found by K. Olschewsky is 138°, and the **critical pressure,** 91 atm.; while R. de Forcrand and H. Fonzes-Diacon gave 137°, and 91 atm. P. Bruylants and J. Dondeyne gave for the **triple point** —65·9° and 203 mm., and for the latent **heat of vaporization,** 4·76 cals. per mol. at —41·2°; while R. de Forcrand and H. Fonzes-Diacon gave 4·74 Cals., and for **Trouton's constant,** 20·52 indicating that the liquid is non-associated. They also emphasized the analogies between the physical constants of hydrogen selenide and sulphide, and the dissimilarities with those of water—*cf.* **1.** 9, 7. M. Berthelot gave for the **heat of formation** (H_2Se_{gas}) $=-2·0$ Cals. R. de Forcrand said that if the mol. of selenium is Se_2 at its b.p., and the latent heat of vaporization 14·805 Cals., $(Se_{gas},H_{2gas})=-4·805$ Cal., but if the constitution of the selenium molecule changes with temp., the heat of formation of hydrogen selenide may become positive. M. Berthelot said that the formation of hydrogen selenide at 0° absorbs heat 5·4 Cals. with β-selenium and 4·2 Cals. with γ-selenium and at 1000° heat is developed. C. Fabre observed that the decomposition of hydrogen selenide by ferric chloride, hydrogen dioxide, and selenium dioxide is attended by the evolution of 18·76, −18·58, and 19·43 Cals. respectively—the mean value for the gas is —18·88 Cals. for vitreous selenium and −13·22 Cals. for metallic selenium. For the heat of formation of the gas from vitreous selenium he gave —18·90 Cals. H. Pélabon calculated —17·38 Cals. L. Rolla obtained for amorphous selenium —16·0256 Cals.; for monoclinic selenium, —17·075 Cals.; and for metallic selenium, −17·455 Cals. The subject was studied by R. de Forcrand. C. Fabre gave 9·26 Cals. for the **heat of solution.** A. J. McAmis and W. A. Felsing found that the heat evolved when a mol of hydrogen selenide is dissolved in water at 25° is 2431 cals.; and the increase of free energy of the reaction $H_2Se_{soln.} \rightarrow H_2Se_{gas}$ at 760 mm. is 1421 cals.

R. de Forcrand and H. Fonzes-Diacon found that purified hydrogen sulphide showed no evidence of decomposition after being kept over mercury for 3 days in darkness, but in **light,** only 15 per cent. remained at the end of 7 days. L. Moser and E. Doctor, however, said that when gaseous or liquid hydrogen selenide is of a high degree of purity, it is not decomposed in daylight, but it is sensitive to **ultra-violet light.** M. G. Weber said that the decomposition of hydrogen selenide, in quartz bulbs exposed to the light from a mercury lamp, begins in two minutes, and the walls of the vessel are very soon covered with a film of selenium. The decomposition is complete.

M. de Hlasko found the mol. **electrical conductivity,** μ, of aq. soln. of hydrogen selenide in an atm. of hydrogen at 25° to be:

	0·1*N*-	0·0249*N*-	0·0137*N*-	0·00817*N*-
μ . . .	17·9	35·3	46·0	59·5
a . . .	0·0424	0·0836	0·1091	0·1410
k . . .	0·000188	0·000190	0·000188	0·000186

The **ionization constant,** k, has the mean value 0·000188; and the **degree of ionization,** a, has the values just indicated. L. Bruner found that an aq. soln. of hydrogen selenide is more acidic than one of hydrogen sulphide; and under atm. press., it is ionized to the extent of 4·1 per cent., and has an **affinity constant** of 0·00017. H. Fonzes-Diacon found that the gas explodes when subjected to **electric sparking,** selenium is deposited, and an equal vol. of hydrogen is produced. M. Berthelot found that with the **silent discharge,** hydrogen selenide is decomposed as in the case of hydrogen sulphide: $8H_2Se=7H_2+H_2Se_n+(8-n)Se$. J. K. Syrkin studied the atomic moments.

J. J. Berzelius analyzed the gas by treating it with silver so as to form silver selenide and hydrogen. The results agreed with the formula H_2Se. A. Bineau obtained similar results by warming hydrogen selenide with tin. R. de Forcrand and H. Fonzes-Diacon said that when hydrogen selenide is of a high degree of purity and quite dry, it is more stable than would be anticipated from its marked endothermal nature. J. J. Berzelius said that the gas forms water and selenium when it comes in contact with **air** and moist substances, and if those substances are porous like paper or wood, they are throughout stained red by the selenium. L. Moser and E. Doctor found that if the dry gas is in contact with dry **oxygen,** there is no reaction, but in the presence of moisture decomposition is rapid. According to A. W. Hofmann, the gas burns with a blue flame, forming, when oxygen is in excess, water and selenium dioxide, and when a lower proportion of oxygen is present, water and selenium are formed. Y. Tanaka and Y. Nagai found that the upper limit of inflammability of mixtures of hydrogen and oxygen is lowered, and the lower limit is raised by admixture with hydrogen selenide or ethyl selenide. J. J. Berzelius said that **water** absorbs the gas more copiously than is the case with hydrogen sulphide, but R. de Forcrand and H. Fonzes-Diacon observed that 100 vols. of water absorb 377 vols. of hydrogen selenide (reduced to n.p. θ) at 4°; 345 vols. at 9·65°; 331 vols. at 13·2°; and 270 vols. at 22·5°. A. J. McAmis and W. A. Felsing found for the solubility of hydrogen selenide at 760 mm. press., in water:

	14·6°	15°	25°	256°	35·0°
Mols per litre .	0·09789	0·09611	0·08415	0·08277	0·07317
C.c. per litre .	2194	2154	1886	1855	1640

The solubility, of S c.c., of hydrogen selenide in a litre of water with hydrogen selenide at 760 mm., between 15° and 35°, can be represented by $S=31940\cdot93-17537T+0\cdot25T^2$. J. J. Berzelius said that with air-free water, the soln. is colourless, and has a faint odour, and hepatic taste; it reddens litmus, and produces a permanent dark-brown stain on the skin. When the soln. is exposed to air, it becomes turbid and red. The change progresses from above downwards, and at length the hydrogen selenide is completely decomposed, and the selenium is precipitated in red flakes. E. Divers and T. Shimidzu added that an aq. soln. of hydrogen selenide is very much more sensitive to the action of air than one of hydrogen sulphide. According to R. de Forcrand and H. Fonzes-Diacon, hydrogen selenide, like hydrogen sulphide, forms colourless crystals of a hydrate, $H_2Se.nH_2O$—probably $H_2Se.6H_2O$. The hydrate does not exist at temp. over 30°. The heat of formation is 16·82 Cals. The vap. press., p, is 760 mm. at 8°, and at

	0°	2·35°	3·40°	5·40°	7·50°	14·1°	22°	30°
p . . .	346	432	490	597	718	1444	3800	8360 mm.

The hydrate seems to form complexes with **alkyl halides.** According to L. Rolla and A. Repetto, the equilibrium conditions in the balanced reaction with **iodine:** $H_2Se+I_2 \rightleftharpoons 2HI+Se$. If p denotes the barometric press., p_1, the vap. press. of iodine, and $p=p_0-p_1-6{\cdot}5$; and C_1, C_2, and C_3 respectively denote the mol. conc. of hydrogen iodide, hydrogen selenite, and hydrogen, $k=(pC_1)^2/(C_1+C_2+C_3)pC_2$, and at 0·1°, log k=4·40711 to 4·40884; at 17°, log k=4·23485 to 4·23628; and at 27°, log k=4·13685 to 4·13801. The heat of this reaction—left to right—is —3·95365 Cals. P. Hautefeuille found that iodine decomposes the aq. soln., forming hydriodic acid, and selenium, which unites with the excess of iodine. A. J. McAmis and W. A. Felsing found that the solubilities of hydrogen selenide at 25° and 760 mm. in **hydriodic acid,** 0·20N-, 0·40N-, and 2·73N-HI, are respectively 1900, 1935, and 2468 c.c. per litre, or 0·08478, 0·08634, or 0·11012 mols per litre. E. Divers and T. Shimidzu observed that when **sulphur,** free from sulphur dioxide, reacts at once with an aq. soln. of hydrogen selenide, or by bubbling the gas through water with sulphur in suspension, the sulphur is instantly coloured superficially, at first orange-red, then deep-red, and lastly, by a prolonged action, dark brown-red. Hydrogen sulphide is simultaneously formed: $H_2Se+S=Se+H_2S$. The reactions between hydrogen sulphide and selenious acid, and between **sulphurous acid** and hydrogen selenide, are rather complex. When a cold, dil. soln. of selenious acid is treated with hydrogen sulphide, a lemon-yellow, pulverulent precipitate is formed containing sulphur and selenium in the proportions 2 : 1. The reaction may be symbolized: $2H_2S+H_2SeO_3 \rightarrow 2S+Se+3H_2O$. If the precipitate is left for some time moistened with carbon disulphide, it forms transparent orange-red scales with the composition SeS, and the excess of sulphur is removed by the solvent. E. Divers and T. Shimidzu continued: If the soln. of selenious acid be warm, the precipitate with hydrogen sulphide is plastic and red, but another reaction also occurs, for sulphuric acid is formed, and the proportion of sulphur in the precipitate is less than 2·1, and this the more the higher the temp. of the soln. The reaction may be represented: $H_2S+2H_2SeO_3=H_2SO_4+2Se+2H_2O$. If hydrogen selenide be passed into a soln. of sulphurous acid, an orange-red precipitate of sulphur and selenium, approximately in the ratio 1 : 2, is formed. When a dil. soln. of sulphurous acid is gradually added, with constant stirring, to a conc. soln. of hydrogen selenide, selenium, quite free from sulphur, is precipitated. The precipitate is at first deep red, but, in the presence of hydrogen selenide, it changes to a brownish-red colour: $3H_2Se+H_2SO_3=3Se+H_2S+3H_2O$; the hydrogen sulphide then reacts with the sulphurous acid depositing sulphur: $2H_2S+H_2SO_3=3S+3H_2O$, and this results in the formation of a precipitate containing a mixture of sulphur and selenium approximately in the proportion 1 : 2. This mixture has been called sulphur diselenide. If an excess of hydrogen selenide be used, the sulphur is attacked as indicated above, and a precipitate of selenium alone is formed. Some seleniothionic acid, but not pentathionic acid, is formed at the same time. H. Pélabon observed that molten **selenium** absorbs hydrogen selenide—*vide supra.* A. Ditte showed that by mixing aq. soln. of **selenium dioxide** and hydrogen selenide, pale-red selenium, soluble in carbon disulphide, is precipitated, and if the precipitate be kept moistened with carbon disulphide for 2 or 3 days, it forms ruby-red crystals of selenium. At an elevated temp., hydrogen selenide and the soln. of selenium dioxide form black selenium.

J. J. Berzelius said that the aq. soln. of hydrogen selenide is not decomposed by a little **nitric acid** in 12 hrs. H. Fonzes-Diacon said that hydrogen selenide does not form a compound with **phosphine**. A. Besson represented the reaction with **phosphoryl chloride** at 100°: $4POCl_3+5H_2Se=10HCl+P_2Se_5+2PO_2Cl$. A. Besson also found that hydrogen selenide is soluble in **carbonyl chloride**; and when a mixture of the two is heated in a sealed tube at 200°, hydrogen chloride and carbon monoxide are formed, and at 230°, the selenium unites with the excess of carbonyl chloride, forming selenium chloride. E. Divers and T. Shimidzu said that hydrogen selenide quickly permeates black, vulcanized **rubber**, turning it red, and this, no doubt, by a reaction with the contained sulphur.

I. Guareschi found that hydrogen selenide is readily absorbed by **soda-lime.** For the action of the gas on various **metal oxides** and **metal salts,** *vide infra*, selenides.

J. J. Berzelius said that selenium unites directly with all the **metals** he tried with the exception of gold, forming **selenides,** analogous to the sulphides. A. Orlowsky observed that selenium has the greatest affinity for the alkali metals; and among the heavy metals it has the greatest affinity for silver; its affinity for copper, mercury, iron, and lead is markedly less; and it is quite small for platinum, chromium, aluminium, and magnesium. E. Obach said that zinc does not act on soln. of selenium in carbon disulphide, tin acts only slowly, while mercury, silver, copper, and lead act readily. Mercury is coloured brown by a soln. of 0·074 grm. of selenium in 20 c.c. of carbon disulphide. R. J. Moss found that if selenium be placed in the vacuum produced by a **mercury** pump, it becomes covered with a conducting film; and a similar result is obtained by dipping a bar of selenium in mercury. According to A. Bineau, impure mercury decomposes hydrogen selenide and at the same time acquires a copper-red coloured film. As indicated in connection with the preparation of hydrogen selenide, the purified gas, in the absence of moisture, does not attack mercury. As shown by J. J. Berzelius—in the case of cerium, manganese, and zinc—soln. of the **metal salts** usually give brown or black precipitates of the selenides (*q.v.*) when treated with hydrogen sulphide.

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§ 7. The Selenides

A. F. Hallimond[1] discussed the isomorphism of the sulphides, selenides, and tellurides. J. J. Berzelius observed that when a mixture of ammonium chloride and calcium selenide is distilled, besides ammonia and selenium, there is formed a red liquid having a strong hepatic odour; when mixed with an excess of water it produces a red turbid mixture; and when exposed to air, ammonia and water are evolved, and selenium precipitated. The composition of the liquid is not known. According to A. Bineau, a mixture of an excess of dry hydrogen selenide and dry ammonia, one vol. of the former unites with one vol. of the latter to furnish a white cloud of **ammonium hydroselenide,** $NH_4.SeH$, the cloud forms a white mass which smells of hydrogen selenide and ammonia. When heated, or exposed to air, it decomposes rapidly with the separation of selenium. C. Fabre gave for the heat of formation of the solid from metallic selenium, $(N,5H,Se)=28{\cdot}85$ Cals.: $(NH_{gas},H_2Se_{gas})=29{\cdot}85$ Cals.; and for the heat of soln. at 18°, $-1{\cdot}99$ Cals. A. Bineau also observed that if an excess of dry ammonia be mixed with dry hydrogen selenide, two vols. of the former unite with one vol. of the latter to produce a white cloud which condenses to a white crystalline mass of **ammonium selenide,** $(NH_4)_2Se$. J. J. Berzelius said that the product is not crystalline. V. Lenher and E. F. Smith found that on sat. with hydrogen selenide a soln. of 5 grms. of ammonium molybdate in 50 c.c. of water to which 20 c.c. of conc. aq. ammonia had been added, a dark red soln. was obtained, from which, on evaporation, black, anhydrous, orthorhombic prisms of ammonium selenide separated. Only from ammoniacal molybdate soln. of the conc. given can the black crystals of ammonium selenide be obtained; under other conditions, selenium alone is formed. The white ammonium selenide of A. Bineau smells of hydrogen selenide and ammonia, and it is more volatile than the hydroselenide. F. A. Flückiger observed that a mixture of ammonium selenide and selenite is formed when selenium and aqua ammonia are heated in a sealed tube. E. Wendehorst prepared the colourless normal selenide by passing purified hydrogen selenide into a sat. soln. of ammonia in an atm. of nitrogen, and cooled to the temp. of melting ice. At higher temp. a complex mixture of ammonium selenides is formed. J. J. Berzelius said that when ammonium selenide is exposed to air, it decomposes with the separation of selenium; and, according to J. J. Berzelius, it forms a red soln. with water. V. Lenher and E. F. Smith added that the black, crystalline product was stable in the air, and dissolved in water to a dark red soln. which gave a precipitate of selenides from neutral or alkaline soln. of metallic salts; the soln., however, gradually decomposed on exposure to the air, selenium being precipitated. According to C. Fabre, the heat of formation of a soln. of the solid from metallic selenium is $(N_2,4H_2,Se)=44{\cdot}48$ Cals.; $H_2Se_{gas}+2NH_{3aq.}=(NH_4)_2Se+15{\cdot}96$ Cals.; $(H_2Se_{aq.},2NH_{3aq.})=6{\cdot}60$, and adding to this the heat of soln. of hydrogen selenide, there remains 15·86 Cals. The addition of a mol of hydrogen selenide to a soln. of ammonium selenide develops 7·0 Cals.

According to G. Calcagni, powdered selenium dissolves readily in the cold in a 66 per cent. soln. of sodium or potassium hydroxide, more slowly in sat. soln. of barium hydroxide on boiling water-bath, and only slowly and in very small proportion in aq. ammonia of sp. gr. 0·888. The soln. thus obtained contain selenides, selenites, and, possibly, a compound analogous to the thiosulphates, formed by the action of atm. oxygen on the selenides; it may be, also, that a small part of the selenium is present as such in the soln. The reactions taking place are gradual and highly complicated, the first products consisting of selenides, which subsequently undergo transformation into polyselenides and selenites. The soln. formed are at first brown, but are gradually decolorized by the combined action of the oxygen and carbon dioxide of the air.

C. Fabre prepared impure **lithium selenide,** Li_2Se, by dehydrating the enneahydrate; by reducing lithium selenate with carbon; and by the action of hydrogen selenide on heated lithium carbonate. Polyselenides appear to be formed at the same time, and the containing vessel is attacked, and the best sample prepared contained 92 per cent. Li_2Se. The reddish-brown product is very hygroscopic, and is decomposed by air. The aq. soln. is red; and the heat of soln., 5·33 Cals. The heat of formation from solid elements is $(2Li,Se)=39{\cdot}63$ Cals. By sat. a conc. soln. of lithium hydroxide with hydrogen selenide—excluding access of oxygen, a liquid is obtained which furnishes colourless, refracting rhombic prisms of the *enneahydrate*, $Li_2Se.9H_2O$. The salt changes quickly if exposed to air, and selenium is separated. The salt is deliquescent. The colourless aq. soln., in air, immediately becomes orange-yellow, and then reddish-brown with the separation of selenium. The salt is very soluble in water; it does not effloresce at ordinary temp. in vacuo. The heat of soln. is —6·10 Cals.

H. Uelsmann found that sodium and selenium unite when heated, and the formation of colourless **sodium selenide,** $NaSe$, is attended by vivid incandescence; but, added C. Fabre, the product probably contained some selenium in consequence of the decomposition of the selenide. If selenium—not in excess—be added to a soln. of sodium in liquid ammonia, C. Hugot found that matt, white, amorphous sodium selenide is precipitated insoluble in liquid ammonia. C. Fabre obtained it by slowly heating the hydrate below 400°. The compound fuses to a reddish-brown liquid, which on cooling becomes a yellow and then a white mass, very hard, and with a crystalline fracture. It turns red on exposure to air, and deliquesces. H. Fonzes-Diacon gave 2·625 for the sp. gr. at 10°. C. Hugot said the m.p. lies above 875°. Owing to the reactivity of the mixture with the containing vessel, C. H. Mathewson could not complete the f.p. curve, Fig. 33, in the region indicated by the dotted line. The m.p. of sodium is lowered very slightly—not more than 0·2° by the addition of selenium. The heat of formation from selenium, and sodium in soln. is $(Na_{soln.},Se_{solid})=39{\cdot}18$ Cals.; $(Na_2O,2H_2Se_{soln.})=3{\cdot}80$ Cals.; and $(Na_2O_{soln.},H_2Se_{soln.})=3{\cdot}56$ Cals. R. Robl observed no fluorescence occurs with the salt in ultra-violet light. H. Uelsmann found that if hydrogen selenide be passed into a conc. soln. of sodium hydroxide, a mush of crystals is formed. They dissolve when the liquid is heated, and the soln. furnishes colourless crystals on cooling. They redden on exposure to air or when heated. L. A. Tschugaeff and V. G. Chlopin obtained sodium selenide by the action of selenium on a soln. of sodium hyposulphite and hydroxide. C. Fabre obtained fine, white needles of the *hemienneahydrate*, $Na_2Se.4\frac{1}{2}H_2O$, by cooling a hot conc. soln. of sodium selenide in conc. soda-lye. The salt reddens if exposed a few seconds to air; it is very deliquescent; and is stable in vacuo at ordinary temp. Its heat of soln. is —3·94 Cals. at 13°. C. Fabre also obtained the *enneahydrate*, $Na_2Se.9H_2O$, by passing a current of hydrogen selenide into a cold soln. of three parts of sodium carbonate and one part of water. A. Clever and W. Muthmann obtained the *decahydrate*, $Na_2Se.10H_2O$, from 10 c.c. of a soln. of equal parts of sodium hydroxide and water, afterwards diluted with a third part of water, and mixed with 6 to 7 grms. of arsenic pentaselenide so as to avoid a great rise of temp. The liquid on standing deposits white needles insoluble in soda-lye, and they can be washed with that medium, and dried on a porous tile. The salt on exposure soon turns rose-red, red, and then brown; and when heated forms a brown liquid. C. Fabre also prepared the *hexadecahydrate*, $Na_2Se.16H_2O$, in white prisms, by passing a current of hydrogen selenide into a soln. of one part of decahydrated sodium carbonate in four parts of water. The crystals melt in their water of crystallization at 40°, and when exposed to air form sodium carbonate, selenium, and a little sodium selenite. The heat of soln. is $-11·0$ Cals. at 14°.

J. J. Berzelius observed that **potassium selenide,** K_2Se, can be formed by the direct union of the elements; the combination is attended by inflammation by which a portion of the selenide is sublimed, and when an excess of potassium is present, there is a kind of explosion. H. Fonzes-Diacon added that if selenium be heated with an excess of potassium, in an iron crucible, the monoselenide is formed and the excess of potassium volatilizes. C. Hugot obtained this selenide by adding the correct amount of selenium to a soln. of potassium in liquid ammonia—the white, amorphous product is insoluble in that menstruum. J. J. Berzelius obtained the selenide by igniting potassium selenite or selenate in an atm. of hydrogen; and J. J. Berzelius, F. Wöhler, and B. Rathke, by igniting a mixture of potassium selenite or selenate and charcoal. J. J. Berzelius also obtained potassium selenide by fusing selenium with potassium hydroxide, or carbonate, whereby some selenite is formed at the same time: $6KOH+3Se=K_2SeO_3+2K_2Se+3H_2O$. C. Fabre also obtained the selenide by dehydrating the enneahydrate. Potassium selenide is a white, crystalline mass which quickly reddens on exposure to air. B. Rathke gave 2·851 for the sp. gr.; and H. Fonzes-Diacon, 2·851 at 15°; the products obtained at the higher temp. may be black, brown, or grey, and possess a hepatic taste and smell. C. Fabre gave for the heat of formation: $(H_2Se_{\text{soln.}},K_2O_{\text{soln.}})=3·76$ Cals.; $(H_2Se_{\text{gas}},K_2O_{\text{soln.}})=8·46$ Cals.; and $2K_{\text{soln.}}+Se_{\text{solid}}=K_2Se_{\text{solid}}+39·71$ Cals. J. J. Berzelius said that when potassium selenide containing an excess of selenium is treated with hydrochloric acid, it swells up, evolves hydrogen selenide, and deposits selenium. When heated, the selenide becomes brownish-black; and when cooled forms a hard, rose-red mass which deliquesces in air, and decomposes into potassium carbonate and selenite, and selenium. C. Fabre treated with hydrogen selenide a soln. of one part of potassium carbonate in 1·5 to 20 parts of water, and obtained a white precipitate which dissolves in the liquid and is transformed into white, needle-like crystals, of the *enneahydrate*, $K_2Se.9H_2O$. This salt rapidly changes in air. It is freely soluble in water, and has a heat of soln. of $-14·65$ Cals. at 14°. If a soln. of one part potassium carbonate in three parts of water is employed, acicular crystals of the *tetradecahydrate*, $K_2Se.14H_2O$, are formed. The heat of soln. is $-10·22$ Cals. at 13°. If the soln. of potassium carbonate is diluted to 1 : 5, crystals of the *enneadecahydrate*, $K_2Se.19H_2O$, are formed with a heat of soln. of $-9·60$ Cals. at 14°. H. Fonzes-Diacon could not confirm the existence of the two latter hydrates. D. M. Liddell said that when exposed to air, selenium and sodium hydroxide are formed. According to J. J. Berzelius, potassium selenide becomes moist in air. When it contains an excess of potassium, it dissolves in water with the evolution of hydrogen and forms a red soln.; if the potassium is not in excess, it forms a dark reddish-brown soln. with water from which acids liberate hydrogen selenide and precipitate selenium. A similar soln. is obtained by boiling selenium for a long time with potash-lye. Soln. of potassium selenide with an excess of selenium with a little water form dark brown soln. from which selenium is precipitated when more water is added. The presence of alkali carbonate prevents the precipitation. All the soln. have a hepatic taste, and on exposure to air deposit selenium as a red powder. When the selenide is treated with selenious acid, B. Rathke said that potassium selenite is formed and selenium precipitated; and C. Fabre added that when treated with hydrogen selenide, **potassium hydroselenide,** KSeH, is formed: $K_2Se_{aq.}+H_2Se_{aq.}=2KSeH_{aq.}+3{\cdot}385$ Cals.

C. L. Jackson said that when sodium selenite is reduced by heating it with carbon, **sodium diselenide,** Na_2Se_2, is formed, and not the monoselenide as in the analogous case of the potassium salt. C. H. Mathewson observed a break in the cooling curves of mixtures containing sodium diselenide corresponding with the decomposition of the diselenide at its m.p. 495°: $Na_2Se_2 \rightleftharpoons Na_2Se+$Melt of composition *B*, Fig. 33. The diselenide is stable in the region represented by the line *BC*. C. H. Mathewson found that **sodium triselenide,** Na_2Se_3, separates as a primary crystalline phase along the short branch of the f.p. curve, *CD*. At 313°, the triselenide melts with decomposition so that it is in equilibrium with the diselenide and the melt of concentration *C*. The quantitative relations are $1Na_2Se \rightleftharpoons 0{\cdot}32Na_2Se_2+$Melt of composition *C*, namely, 1·35 mols of Na, and 2·35 mols of Se. A. Clever and W. Muthmann obtained **potassium triselenide,** $K_2Se_3.2H_2O$, in brown needles, when potassium selenide is mixed with arsenious acid dissolved in alkali; the crystals rapidly decompose and become coated with grey selenium on exposure to air. It dissolves in water, and the soln., when treated with acids, yields selenium and hydrogen selenide. C. Hugot observed that if an excess of selenium is treated with a soln. of sodium in liquid ammonia, a brown soln. is formed, and if the solvent is evaporated off at —25°, and the residue cooled to —55°, **sodium tetraselenide,** Na_2Se_4, is formed. If a soln. of potassium in liquid ammonia be treated in an analogous way, **potassium tetraselenide,** K_2Se_4, is formed. The brown mass dissolves in water, forming a violet soln., and in liquid ammonia, forming a brown soln. The aq. soln. deposits selenium on exposure to air; and when treated with acids, hydrogen selenide is given off with the separation of selenium. C. H. Mathewson found that in the Na–Se system, sodium tetraselenide crystallizes primarily along the flat curve *DE*, Fig. 33. It melts with decomposition at 290°, owing to the reversible action: $1Na_2Se_4 \rightleftharpoons 0{\cdot}4Na_2Se_3+$Melt of composition *D*, namely, 1·20 mols of Na and 2·80 mols of Se. F. W. Bergstrom prepared **sodium pentaselenide,** Na_2Se_5, and **potassium pentaselenide,** K_2Se_5, as well as the other polyselenides. There is no indication of the formation of *sodium pentaselenide,* Na_2Se_2, on the f.p. curve; but **sodium hexaselenide,** Na_2Se_6, appears as the primary crystalline phase separating along the branch between *E* and the m.p. of selenium. The hexaselenide melts with decomposition at 258°, when there is the reversible action $1Na_2Se_6 =0{\cdot}73Na_2Se_4+$Melt of composition *E*, namely, 0·54 mol of Na and 3·08 mol of Se. There is no sign of the existence of a higher polyselenide. After the heating and supercooling of grey, metallic selenium, crystallization does not take place, but the substance gradually solidifies to an amorphous mass. The addition of 0·1 per cent. of sodium is sufficient, however, to cause complete crystallization at 217°. The solubility of sodium hexaselenide in selenium at its m.p. is extremely small, but the limited miscibility may be the cause of the crystallization. Polyselenides are darker than grey, metallic selenium, become red and disintegrate on exposure to air in consequence of the separation of selenium, and are readily soluble in water, forming red soln., the depth of colour increasing with the amount of selenium.

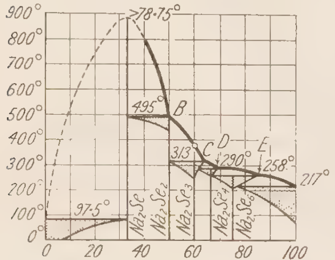


Fig. 33.—Freezing-point Curve of the Binary System: Sodium–Selenium.

A. Orlowsky[2] found that the affinity of copper for selenium is greater than is that of the other heavy metals with the exception of silver. A. L. Potilitzin found that in a sealed tube at 600°–700°, selenium will displace 48·01 per cent. of sulphur from cuprous sulphide. K. Friedrich and A. Leroux made a partial exploration of the equilibrium diagram of the system: copper–selenium. The addition of selenium lowers the f.p. of copper to the eutectic at 1063° with 2 to 3 per cent. of selenium. The curve then rises, Fig. 34, soon becoming nearly horizontal, owing to the separation of two liquid layers whose limits were not exactly determined. The existence of cuprous selenide, m.p. 1113°, is indicated. Copper does not form solid soln. with selenium.

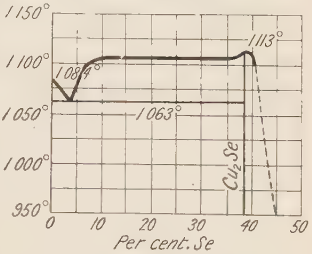


Fig. 34.—Freezing-point Curve of the Binary System: Copper–Selenium.

J. J. Berzelius described a mineral from Skrikerum, Sweden, which he called Selenkupfer, and the analysis agreed, fairly well, with that required for **cuprous selenide,** Cu_2Se. A. E. Nordenskjöld found that it contained 4·73 to 8·50 per cent. of silver, 0·35 to 0·54 per cent. of iron, and up to 0·38 per cent. of thallium. A. de Gramont found, spectroscopically, silver, lead, thallium, and magnesium, as well as copper and selenium. T. Parkman analyzed artificial cuprous selenide. The mineral was also described by W. Hisinger, and A. E. Nordenskjöld. F. S. Beudant called it *berzeline*—after J. J. Berzelius—and J. D. Dana altered this term to **berzelianite.** Occurrences at Lerbach, Harz, were described by J. C. Zimmermann, G. Frebold, J. R. Blum, O. Luedecke, and F. A. Römer; and at Andreasberg, by H. Rose, and W. Geilmann and H. Rose. J. J. Berzelius made cuprous selenide by heating a mixture of copper and selenium—the combination was attended by incandescence—and also by heating cupric selenide to redness in a closed vessel. J. Margottet, and S. Bidwell made cuprous selenide by the action of selenium vapour on copper. H. Fonzes-Diacon obtained it by the action of hydrogen on red-hot cupric selenide, also by the action of carbon on cupric selenate at a high temp. in a vessel protected from air; by the action of hydrogen selenide on a soln. of cuprous chloride in hydrochloric acid, and rapidly washing the product first with hydrochloric acid, and then with air-free water; and by the action of a mixture of hydrogen and hydrogen selenide on anhydrous cuprous or cupric chloride at a red-heat. L. Moser and K. Atynsky obtained it by the action of a soln. of a potassium cuprous salt on a soln. of hydrogen selenide out of contact with air. T. Parkman prepared it by the action of selenium and sulphur dioxide on a soln. of a cupric salt, and A. Brukl by precipitation. F. Garelli obtained crystals of copper selenide by wrapping a piece of selenium with copper wire and immersing it in a soln. of copper sulphate. P. Fischer obtained metal selenides by electrolyzing a soln. of sodium sulphate with a selenium cathode, and an anode of the given metal.

Cuprous selenide is described as a bluish-black, dark green, steel-grey, or a black powder, or when it has been fused, as a crystalline mass with a compact fracture. The grains are cubic, octahedral, or tetrahedral. W. P. Davey found that the X-radiogram agreed with two interpenetrating face-centred cubic lattices—calcium fluoride type—of side 5·751 A., and density 7·154. W. Hartwig also found the selenideh as a face-centred lattice of the fluorite type with 4 mols. Cu_2Se per unit cell. The natural selenide has a cell with side a=5·731 A. and the artificial, a=5·748 A. L. Pauling, and E. J. Guy discussed the spectral relations of the atoms. M. L. Huggins studied the atomic structure. F. Rössler dissolved the powder in molten lead, and extracted the lead from the cold mass by cold, dil. nitric acid, and the residue, under the microscope, contains reddish-yellow and steel-grey octahedra, feathery crystallites, and copper-coloured rhombic plates. The mineral berzelianite occurs disseminated as a black or bluish-black powder in calcite of Skrikerum or else in thin, silver-white, dendritic crusts. J. C. L. Schröder van der Kolk said that the streak is pale brownish-grey. The metallic lustre of the mineral soon tarnishes. The sp. gr. of the mineral is 6·71; M. Bellati and S. Lussana gave for the sp. gr. of cuprous selenide 6·749 at 30·25°/4°, and H. Fonzes-Diacon, 6·512. K. Friedrich and A. Leroux gave 1113° for the m.p. S. Lussana said that there is a transition temp.

at 110°, and that the heat of the transformation is 5·405 cals. J. Joly found that the mineral gives a white sublimate at 440° in air. A. Beutall obtained hair copper by heating the selenide in a sealed tube at 350°–400°. H. Fonzes-Diacon gave 20·84 Cals. for the heat of formation of the crystalline selenide, and 9·7 Cals. for the precipitated. A. de Gramont studied the spark spectrum. H. E. McKinstry observed no effect when the mineral is exposed to the electric arc-light. J. W. Hittorf, J. W. Clark, and M. Bellati and S. Lussana found that cuprous selenide conducts electricity like a metal. M. Bellati and S. Lussana said that as the temp. rises from 23·3° to 98·8°, the electrical resistance increases from 0·0427 to 0·06669 ohm; and as the temp. rises to 127·3°, it falls to 0·04651; rising again to 0·05148 as the temp. reaches 161°. The resistance is not altered by blue-light. T. W. Case also said that the resistance is not affected by light. S. Bidwell thought that the increased conductivity of selenium in light is conditioned by the presence of copper selenide, but this hypothesis had to be abandoned—*vide supra.* However, cuprous selenide lowers the resistance of selenium, and also its sensibility to light, although non-sensitive selenium becomes sensitive when alloyed with cuprous selenide. F. T. Snyder used the selenide as a material for resistance coils. A. L. Williams measured the resistance of fused mixtures of selenium and copper. M. Bellati and S. Lussana found that the thermoelectric force of the copper selenide and lead thermocouple, as the current passes from the lead through the hot junction to the cuprous selenide, is $0{\cdot}0_{3}19$ volt at 30°, and 0·00844 volt at 160°. S. Bidwell said that if cuprous selenide be placed between two sheets of moist paper to act as electrodes, when a current is passed, selenium appears on the anode-paper, and copper on the cathode paper; and O. Weigel added that cupric selenate is also formed at the cathode and hydrogen selenide at the anode. E. T. Wherry found that berzelianite is a fair radio-detector; and I. Stransky discussed the rectifying action of the heavy metal selenides. J. J. Berzelius found that when cuprous selenide is heated for a long time in air, part of the selenium is driven off, leaving brittle, fusible, seleniferous copper. Berzelianite is soluble in conc. nitric acid. H. Fonzes-Diacon observed that cuprous and cupric selenides are decomposed by hydrogen chloride either in soln. or at high temp., in the former case, hydrogen selenide being evolved; they are readily attacked by chlorine, oxidized to cupric selenite by nitric acid and dissolved by sulphuric acid with the evolution of sulphur dioxide. Ammonia attacks the cuprous selenide rather more readily than the cupric compound, whilst both substances are partially soluble in ammonium hydrosulphide. Cuprous selenide is soluble in a soln. of potassium cyanide, and E. Heyn and O. Bauer, and F. W. Hinrichsen and O. Bauer detected cuprous selenide in copper by warming the metal with an aq. soln. of potassium cyanide, and adding alcohol, and an acetic acid soln. of cadmium acetate when an orange-red precipitate indicated the presence of selenium. K. B. Rogers found that berzelianite is decomposed by heating it 10 min. at 250° to 300°, and 20 min. at 375° to 425° in the vapour of carbon tetrachloride and air. C. Tubandt and H. Reinhold studied the reaction: $Ag_2S + Cu_2Se \rightleftharpoons Cu_2S + Ag_2Se$.

F. Klockmann described a mineral which he named **umangite**; it occurs at the Sierra de Umango, La Rioja, Argentina, in dark cherry-red granular or compact masses, without cleavage. The fresh fracture has a violet tinge, but it soon tarnishes, and the colour appears violet-blue. The analysis corresponds with **cuprosic selenide,** Cu_3Se_2, or $Cu_2Se.CuSe$; C. F. Rammelsberg gave $2Cu_2S.CuSe$; and P. Groth and K. Mieleitner, $(Cu,Ag)_3Se_2$. Umangite thus resembles an earth previously obtained by F. Pisani from South America. J. Olsacher, and G. Frebold found it in the Harz; and H. Rose, and W. Geilmann and H. Rose, in Andreasberg. The sp. gr. is 5·62, and the hardness 3. R. G. Harvey measured the electrical resistance. J. J. Berzelius said that **cupric selenide,** $CuSe$, is precipitated when hydrogen selenide is passed into a soln. of cupric sulphate. L. Moser and K. Atynsky also prepared this compound in an analogous way. G. Little said that cupric selenide is formed when selenium vapour is passed over heated copper; J. Margottet, when selenium vapour in a current of nitrogen is passed over copper at a red-heat; H. Fonzes-Diacon, by passing hydrogen selenide over anhydrous cupric chloride at 200°; and J. E. Gerock obtained it as a residue when copper is dissolved in seleniferous hydrochloric acid. P. Ramdohr regarded umangite as a new mineral, cupric selenide, and he called it *klockmannite.* G. Little analyzed cupric selenide, and added that the sp. gr. is 6·665, whilst H. Fonzes-Diacon gave 5·398 for the sp. gr. at 15°. Cupric selenide forms long bluish-black, prismatic needles, which, according to H. Fonzes-Diacon, melt at a dull red-heat. J. J. Berzelius, and H. Fonzes-Diacon said that the selenide loses half its selenium at a red-heat. Some chemical reactions are indicated in connection with cuprous selenide. C. Fabre gave 9·70 Cals. for the heat of formation of the precipitate. H. E. McKinstry observed no effect when the mineral is exposed to the electric arc-light.

A. Orlowsky [3] found that of the heavy metals silver has the greatest affinity for selenium; and, as shown by J. J. Berzelius, alloys of the two elements are readily obtained by fusion, and silver is blackened by selenium vapour, selenium dioxide, and hydrogen selenide. H. Pélabon found that mixtures of silver and selenium containing from 5 to 60 per cent. of silver separate at 620° into two layers, the upper consisting of pure selenium, the lower of a mixture of silver and selenium in atm. proportions; as the proportion of silver is increased the solidifying points rise to 880°, the m.p. of the selenide Ag_2Se; the eutectic mixture melts at 830° and contains 80·5 per cent. of silver. K. Friedrich and A. Leroux added that mixtures of silver with more than 7 per cent. Se separate into two liquid layers. The existence of the selenide Ag_2Se with a m.p. between 834° and 850°, is indicated, but mixtures richer in selenium could not be prepared, owing to loss by volatilization. G. Pellini observed that the f.p. diagram, Fig. 35, shows that with increasing proportions of silver, the f.p. curve of selenium rises rapidly from the m.p. of selenium, 217°, to 616°; and then remains horizontal with between 45 and 52 at. per cent. of silver; beyond that, the f.p. rises rapidly to a maximum at 897° with 66·6 at. per cent. of silver, *i.e.* with **silver selenide,** Ag_2Se. Next, there is a sharp fall to 845° with 67·5 at. per cent. of silver; this is followed by a rise to 890° when the temp. remains steady with from 68 to 89 at. per cent. of silver. Finally, the curve rises to the m.p. of silver. There is here no evidence of the **silver diselenide,** Ag_2Se_2, stated by J. J. Berzelius to be formed when silver selenide is heated with an excess of selenium and the excess removed by heating the product out of contact with air.

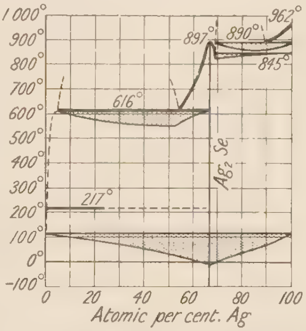


FIG. 35. Freezing Points of Mixtures of Silver and Selenium.

G. Rose found a mineral at Tilkerode, Harz, whose analysis corresponded with the selenide, Ag_2Se, or with silver lead selenide, $Ag_2Se.5PbSe$, according to analyses by C. F. Rammelsberg, and I. Domeyko, and Ag_2Se, according to E. V. Shannon. G. Rose called it *Selensilber;* E. F. Glocker, *Selensilberglanz* or *Selensilberbleiglanz;* and W. Haidinger, **naumannite** after C. F. Naumann. Occurrences in the Harz were also described by J. C. L. Zincken, G. Frebold, and O. Leudecke; in Mexico, by A. M. del Rio, and C. F. de Landero; in Andreasberg, by H. Rose, and W. Geilmann and H. Rose; in Idaho, by E. V. Shannon; and a mineral from Cacheuta, Mexico, analyzed by I. Domeyko, was called by M. Adam *cacheutaite.* I. Domeyko regarded cacheutaite as a mixture of $(Ag,Cu)_2Se$, $(Fe,Co)Se$, and $PbSe$.

According to J. J. Berzelius, silver selenide, Ag_2Se, is prepared by melting together the constituent elements in the correct proportions; and by passing hydrogen selenide into a soln. of silver nitrate, and drying the black precipitate. J. Margottet obtained the selenide by heating silver in the vapour of selenium mixed with nitrogen. J. B. Senderens found that selenium readily acts on a boiling soln. of silver nitrate: $4AgNO_3+3Se+3H_2O=2Ag_2Se+H_2SeO_3+4HNO_3$; and R. D. Hall and V. Lenher observed that the reaction occurs with a cold soln. T. Parkman said that red selenium is blackened by a soln. of silver nitrate, forming flakes of selenium dioxide, but, added R. D. Hall and V. Lenher, this is a mistake since selenium dioxide is readily soluble in water; the white precipitate was probably silver selenite. H. Fonzes-Diacon could not make *silver diselenide*, Ag_2Se_2, and said *il ne parait donc pas devoir exister.* P. Fischer made the selenide by electrolysis—*vide* copper selenide. L. Moser and K. Atynsky obtained black, unstable silver selenide, Ag_2Se, by the action of a silver salt on a soln. of hydrogen selenide out of contact with air; the product loses selenium on drying, and forms complex salts with alkali hydroxides, sulphides, and selenides. F. Garelli and A. Angeletti could not confirm P. Guyot's statement that from neutral or acid soln. of salts of the metals, selenium dissolved in carbon disulphide precipitates only silver as silver selenide. In aq. soln. the silver may be precipitated completely if excess of selenium is used and the liquid is boiled, the reaction corresponding with the equation: $4AgNO_3+3Se+3H_2O=2Ag_2Se+H_2SeO_3+4HNO_3$, as indicated by J. B. Senderens. The silver may be completely precipitated in this way from soln. containing silver, lead, and mercury salts, provided the selenium added is twice the amount of the silver present. J. Margottet described silver selenide as a lead-grey powder consisting of microscopic needles of hexagonal form. F. Rössler said that the selenide dissolves in molten silver or bismuth without suffering chemical change, for if the cold mass be treated with cold, dil. nitric acid, or acetic acid, dendrites, and dodecahedral crystals of the selenide are formed. Naumannite occurs in black, cubic crystals, as well as in granular or compact masses, or in thin plates. The cubic cleavage is perfect. L. S. Ramsdell studied the X-radiogram. M. L. Huggins studied the atomic structure of the crystals. G. Rose gave for the sp. gr. 8·0. H. Fonzes-Diacon gave for the artificial selenide 8·216 at 15°; and M. Bellati and S. Lussana gave 7·952 at 30·1°/4° for the sp. gr., F. A. Henglein, 26·9 for the mol. vol. M. Bellati and S. Lussana gave 0·06836 for the sp. ht. G. Rose gave 2·5 for the hardness of naumannite; and J. Margottet said that silver selenide is soft enough to be cut with a knife. N. A. Puschin said that the silver selenium alloys are almost black, crystalline, and harder than either component; and H. Rössler, and H. Debray said that the presence of small proportions greatly influence the physical properties of silver—one per cent. of selenium makes silver useless for many purposes. M. Bellati and A. Leroux found that there is a transition point at 133°, when the sp. ht. changes to 0·06843. The heat of the transformation is said to be 5·631 Cals. J. J. Berzelius said that silver selenide melts at a red-heat without the loss of selenium and forming a silver-white, ductile mass; J. Margottet found that selenium separates out at a white-heat. H. Pélabon gave 880° for the m.p.; K. Friedrich and A. Leroux, between 834° and 850°; and G. Pellani, 897°—Fig. 35. A. Beutall obtained hair silver by heating the selenide in a sealed tube at 300°–600°. C. Fabre gave for the heat of formation of the crystals from solid selenium 4·72 Cals., and for the precipitate, 2·48 Cals. H. E. McKinstry observed no effect when naumannite is exposed to the electric arc-light. F. Beijerinck, and R. G. Harvey stated that naumannite is a conductor of electricity; and M. Bellati and S. Lussana observed that silver selenide is not electrolyzed by the passage of the current. The electrical resistance at 25·6° is 0·02033 ohm, rising to 0·02240 ohm at 100°, remaining constant to 120°; it then increases rapidly to 0·02549 ohm as the temp. rises to 137°, and slowly to 0·02742 ohm at 200·4°. F. Beijerinck found that naumannite is a conductor of electricity. M. Bellati and S. Lussana found that the thermoelectric force of the silver selenide and lead couple is 0·00023 volt at 30°; 0·00209, at 60°; 0·00405, at 90°; 0·00593, at 120°; 0·00669, at 140°; 0·00759, at 160°; and 0·00838, at 180°. The current passes from the selenide to the lead through the hot junction. N. S. Puschin measured the e.m.f. of the cell $Ag \mid 0{\cdot}143N\text{-}AgNO_3 \mid Ag_2Se_n$ for different values of n, and found that the potential of the mixture is nearly constant and equal to that of pure silver until n is unity, when there is a sudden drop in potential; corresponding with Ag_2Se, Fig. 36; after this further additions cause little change in the potential. E. T. Wherry found naumannite to be a poor radiodetector. J. Margottet found that hydrogen reduces silver selenide at a red-heat, forming filiform silver. According to H. Pélabon, while silver readily attacks hydrogen selenide, and when in excess decomposes it entirely, on the other hand, the action of hydrogen on heated silver selenide is very slight, even at 620° the decomposition is inconsiderable, and after 48 hrs. the ratio of gaseous hydride to total hydrogen is only 1·01. J. J. Berzelius said that when the selenide is heated in air for a long time it does not part with all its selenium, nor does it do so even when fused with alkalies, or iron. H. Fonzes-Diacon said that when the selenide is heated in oxygen it forms metallic silver and selenium dioxide; chlorine transforms it into silver and selenium chlorides; conc. hydrochloric acid attacks it at the beginning, forming a layer of silver chloride which protects it from further attack; and fuming nitric acid converts it into selenite without the loss of hydrogen selenide. J. J. Berzelius added that boiling acid dissolves the selenide, forming silver selenite which separates out in crystals on cooling, or in a pulverulent form when treated with water. G. Rose added that naumannite is but slowly attacked by dil. nitric acid, but dissolves fairly quickly in the fuming acid. J. J. Berzelius said that iron unites with silver selenide, forming a dark grey, granular mass. H. Pélabon said that 0·05 mol of the sulphides of arsenic, antimony, or bismuth per mol of silver selenide, lowers the m.p. from 880° to 790°. R. Marc noted that the presence of a trace of silver selenide, say 0·03 per cent., hastens the speed at which selenium attains equilibrium in light. G. Tammann studied the chemical activity of the silver-selenium alloys; and C. Tabandt and H. Reinhold, the reaction $Ag_2S+Cu_2Se \rightleftharpoons Cu_2S+Ag_2Se$.

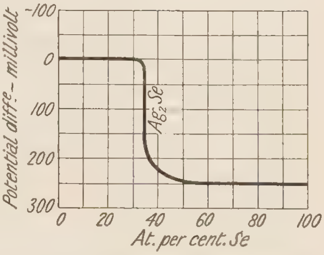


FIG. 36.—Potential Difference in the Cell: Ag | $\frac{1}{7}N$-$AgNO_3$ | AgSe.

The mineral **aguilarite**—named after Senor Aguilar—from a mine at Guanajuato, Mexico, was described by F. A. Genth. Analyses agree with the formula Ag_4SeS, or $Ag_2S.Ag_2Se$, **silver selenosulphide,** or, according to C. F. Rammelsberg, $Ag_4(S,Se)_2$, or $mAg_2S.mAg_2Se$. It furnishes iron-black, skeleton dodecahedra which are often elongated in the direction of a cubic or octahedral axis. There is no cleavage. Its sp. gr. is 7·586, and its hardness 2·5. An alteration product resembles a cupriferous stephanite. H. E. McKinstry observed no effect when the mineral is exposed to the electric arc-light. R. G. Harvey measured the electrical resistance. E. T. Wherry said that aguilarite is a fair radiodetector.

J. J. Berzelius described a **copper silver selenide,** $Cu_2Se.Ag_2Se$, occurring in a copper mine at Skrikerum, Sweden, and it was called **eucairite**—from εὐκαίρως, opportunely, in allusion to its discovery soon after that of the element selenium. Its occurrences in Sweden were also described by W. Hisinger, and A. E. Nordenskjöld; in the Siebenbürge, by V. R. von Zepharovich, and J. M. Ackner; in Chili, by I. Domeyko; and in the Argentine, by G. Fromme, R. Otto, and F. Klockmann. Analyses were reported by J. J. Berzelius, A. E. Nordenskjöld, I. Domeyko, G. Fromme, and F. Klockmann. C. F. Rammelsberg gave for the composition $Ag_2Se.Cu_2Se$. J. Meyer and H. Bratke said that this is the only double selenide containing two different heavy metals whose existence is known with certainty. J. Margottet prepared artificial octahedral crystals by the method used for the simple sulphides. F. Fouqué and A. Michel-Lévy discussed this subject. L. S. Ramsdell studied the X-radiogram. The colour of eucairite is silver-white or lead-grey. It occurs massive, granular, and in black films. The crystals are cubic. The sp. gr. is 7·50, and the hardness 2·5. J. Joly observed a red sublimate at 380° in air, and a white sublimate at 410°. A. de Gramont studied the spark spectrum. The mineral is soluble in boiling nitric acid.

J. J. Berzelius, H. Pélabon, and H. Uelsmann found that gold does not unite with selenium when the elements are heated together. N. W. Fischer observed that selenium reduces a soln. of a gold salt at a high temp. R. D. Hall and V. Lenher also showed that selenium has no action on soln. of gold salts unless heated nearly to boiling when the reaction: $3Se+4AuCl_3=3SeCl_4+4Au$, occurs. L. Moser and K. Atynsky obtained black, unstable **aurous selenide,** Au_2Se, by the action of a potassium aurous salt on a soln. of hydrogen selenide protected from air; with an auric salt, black **auric selenide,** Au_2Se_3, is formed; and H. Fonzes-Diacon represented the reaction with hydrogen selenide when the soln. is cold: $2AuCl_3+3H_2Se=2Au+3Se+6HCl$; and when the soln. is hot there is a further reaction: $2AuCl_3+Se+4H_2O=H_2SeO_4+6HCl+2Au$. F. Osmond and W. C. Roberts-Austen made observations on the structure of the alloy. H. Uelsmann obtained **gold selenide,** Au_2Se_3, by passing hydrogen selenide into an aq. soln. of gold chloride. Light is to be excluded or the precipitate will be mixed with gold. The black, amorphous selenide has a sp. gr. 4·65 at 22°; and when heated, the selenium can be expelled. M. L. Huggins studied the atomic structure. When gold selenide is heated with mercury, mercuric selenide is formed. A. Steigmann studied the so-called gold-selenium toning in photography. A. Beutall obtained hair gold by heating the selenide in a sealed tube at 350°–600°. Gold selenide is soluble in aqua regia, and soln. of alkali sulphides; nitric acid dissolves the selenium; and sulphur dioxide precipitates selenium and gold from the soln. in aqua regia. The product may have been a mixture.

J. J. Berzelius prepared **calcium selenide,** CaSe, by heating calcium selenate to redness in hydrogen; and C. Fabre reduced the selenate, dried at 200°, in a current of hydrogen at dull redness. H. Fonzes-Diacon made calcium selenide by the action of selenium vapour on heated calcium; or by the action of hydrogen selenide on calcium-ammonium; and F. A. Henglein made the alkaline earth selenides by reducing the corresponding selenates in a stream of hydrogen at 400° for the calcium salt, 690° for the strontium salt, and 500° for the barium salt. M. K. Slattery used this process for strontium selenide. According to J. J. Berzelius, a soln. of potassium selenide gives a flesh-coloured precipitate when added to a soln. of calcium chloride. If a soln. of calcium hydroxide be sat. with hydrogen selenide and kept out of contact with air, dark brown crystals of calcium selenide are formed. W. P. Davey found from the X-radiograms that calcium selenide has a space lattice of simple cubical structure with side $a=2·957$ A.; and M. K. Slattery obtained similar results with strontium selenide with side 3·117 A., and barium selenide with side 3·308 A. I. Oftedal gave $a=5·912$ A., and H. Haase, $a=5·914$ with the ionic distances 2·957 A. L. Pauling made some observations on this subject. F. A. Henglein and R. Roth gave 3·57 for the sp. gr. of calcium selenide, 4·38 for strontium selenide, and 5·02 for barium selenide; and H. Haase, 3·81, 4·54, and 4·94. F. A. Henglein gave for the mol. vols. of calcium, strontium, and barium selenides respectively 33·2, 37·4, and 43·5; H. Haase respectively 31·31, 36·74, and 43·85; and J. Geissler respectively 33·2, 38·1, and 43·5. C. Fabre gave for the heat of formation (Ca,Se)=39·0 Cals.; and $(CaO,H_2Se_{gas})=4·88$ Cals.; and 17·4 Cals. for the heat of soln. in dil. hydrochloric acid at 15°. K. Spangenberg found the index of refraction to be 2·274, and the mol. refraction 18·24; H. Haase found the index of refraction for the Tl-, *D*-, and *C*-lines to be respectively 2·302, 2·274, and 2·245, and the mol. refraction 18·22. F. A. Henglein and R. Roth said that the alkaline earth selenides are white, microcrystalline powders, of cubic habit. They become brown on exposure to air, and are decomposed by water. J. J. Berzelius, and C. Fabre prepared **strontium selenide,** SrSe, in a similar way—*vide supra;* and C. Fabre gave for the heat of formation $(SrO,H_2Se_{gas})=10·29$ Cals.; and for the heat of soln. in dil. hydrochloric acid at 15°, 16·82 Cals. K. Spangenberg gave 2·220 for the index of refraction, and 20·81 for the mol. refraction; H. Haase gave for the index of refraction respectively for the Tl-, *D*-, and *C*-lines, 2·255, 2·220, and 2·190, and 20·83 for the mol. refraction. J. J. Berzelius prepared **barium selenide,** BaSe,—*vide supra*—whose heat of refraction is $(BaO,H_2Se_{gas})=10·13$ Cals.; and the heat of soln. in dil. hydrochloric acid at 15° 16·95 Cals. H. Haase gave for the index of refraction, respectively for the Tl-, *D*-, and *C*-lines, 2·307, 2·268, and 2·237, and for the mol. refraction, 25·43. R. Robl observed no fluorescence occurs with barium selenide in ultra-violet light. Barium selenide rapidly reddens when exposed to air. The pure selenide does not phosphoresce after it has been exposed to light. H. Moser, and W. E. Pauli found that phosphorescent preparations of alkaline-earth metal selenides can be obtained by methods similar to those employed for the preparation of the active sulphides. The phosphorescent selenides actually obtained are represented by the formulæ: Ca(Bi)Se, Sr(Cu)Se, Sr(Bi)Se, Sr(Pb)Se, Ba(Pb)Se, and Ba(Cu)Se, where the bracketed symbol refers to the metallic "impurity" present. The sensitiveness of the phosphorescence of the selenides to small variations in the conditions of formation—for instance, in the temp. to which they are heated, the period of heating, the admission or exclusion of air, and the rate of cooling—is more pronounced than that of the active sulphides. For the same metallic "impurity," the number of bands in the spectra of the selenides is smaller than in the spectra of the corresponding sulphides. The upper temp. limit, above which the active substances do not show any after-luminosity, is also much lower for the selenides than for the sulphides. Certain heavy metals which act as the photo-electrically sensitive constituents in the case of the alkaline-earth metal sulphides are incapable of exciting phosphorescence if present in the selenides. F. Kittelmann studied the phosphorescence of the alkaline earth selenides. K. Spangenberg gave 2·268 for the index of refraction, and 25·45 for the mol. refraction. H. Fonzes-Diacon found that oxygen oxidizes calcium selenide with incandescence, forming the selenite. The selenide is decomposed by water. Chlorine displaces the selenium from the warm selenide, and bromine and iodine act similarly, but at a higher temp. —dull redness. Hydrochloric acid furnishes hydrogen selenide; dil. sulphuric acid also gives hydrogen selenide; but with the conc. acid, selenium is set free; and with the hot fuming acid, a green liquid is formed with the evolution of sulphur dioxide. Fuming nitric acid dissolves the selenide without loss of selenium, forming the selenite. J. J. Berzelius supposed that aq. soln. of calcium hydroxide sat. with hydrogen selenide contained **calcium hydroselenide,** $Ca(SeH)_2$. When selenium is heated to redness with calcium oxide, there remains a pale brown mixture of **calcium polyselenide** and selenite; the brown, coke-like mass has no taste or smell, and it is insoluble in water, and when heated to a red-heat, selenium is given off and the monoselenide remains. It is decomposed by acids with the separation of selenium; no hydrogen selenide is evolved, since this is decomposed by the selenious acid also present. A soln. of potassium selenide gives a flesh-coloured precipitate with strontium salts. The resulting **strontium polyselenide** does not lose selenium at a red-heat; but when decomposed by acids, selenium is deposited. Similarly also with **barium polyselenide.**

According to F. Wöhler,[4] beryllium and selenium unite when strongly heated, forming a brittle, crystalline mass of **beryllium selenide,** presumably BeSe; but C. L. Parsons said that he was probably mistaken. W. Zachariasen found that the space lattice of beryllium selenide is a face-centred cube of side $a=5·129$ A. H. Haase gave 5·43 A., and for the ionic distances, 2·715 A. According to J. J. Berzelius, ammonium selenide gives a flesh-coloured precipitate of the selenide when added to a soln. of a beryllium salt; and with magnesium salts, **magnesium selenide,** presumably MgSe, is formed in a similar way. The selenide gives off selenium when ignited and selenium is deposited when the selenide is treated with acids. D. M. Liddell made magnesium selenide by dropping selenium into molten magnesium, and H. Fonzes-Diacon, by the action of the vapour of selenium, carried in a current of nitrogen on powdered magnesium. The action is slow, and the product impure. The reaction between selenium and magnesium powders, intimately mixed, is violent. The best results were obtained by the action of hydrogen selenide on anhydrous magnesium chloride at a red-heat. L. Moser and K. Doctor obtained magnesium selenide by passing selenium vapour over the metal heated in vacuo; and by igniting a mixture of the component elements by means of a burning magnesium wire. The light brown powder is unstable in air. E. Broch found the X-radiogram agreed with a face-centred cube lattice of side a=5·452 A., and a sp. gr. 4·21—*vide* magnesium telluride. G. Bruni and A. Ferrari made observations on this subject. H. Haase gave 4·27 for the sp. gr., and 24·24 for the mol. vol. F. A. Henglein gave 24·4 for the mol. vol.; and J. Geissler, 24·4. K. Spangenberg gave for the index of refraction 2·42, and for the mol. refraction, 15·0. H. Haase gave for the index of refraction for the *D*-line, 2·42, and for the mol. refraction, 15·12. H. Fonzes-Diacon said that magnesium selenide is not reduced by heating it in a current of hydrogen, or when admixed with carbon. When exposed to air, the moisture reacts, forming hydrogen selenide; and with a little water, the selenide gives off hydrogen selenide, and with a large excess of water it gives a precipitate of magnesium hydroxide, without the evolution of gas. The supernatant liquid seems to contain a soluble **magnesium hydroselenide,** because it gives off hydrogen selenide when treated with acids. Acids easily decompose magnesium selenide, and nitric acid converts the selenide into selenite without loss. Chlorine displaces the selenium, and bromine and iodine vapours do the same at a higher temp.

According to J. J. Berzelius, a pale red precipitate of hydrated **zinc selenide,** presumably $ZnSe$, is formed by mixing soln. of a zinc salt and potassium selenide. H. Rose, and W. Geilmann and H. Rose observed its occurrence at Andreasberg. It is insoluble in water, and decomposed in air, becoming dark red. He found that zinc and selenium combine very imperfectly when fused together; most of the selenium volatilizes, and a film of sulphur-yellow selenide forms on the surface of the metal; but zinc selenide, $ZnSe$, is readily formed, without explosion, when the vapour of selenium is passed over zinc at a red-heat. L. Moser and E. Doctor passed selenium vapour over the metal heated in vacuo. M. Chikashige and R. Kurosaura found that the fused elements are not appreciably miscible, and the selenide does not dissolve in either element. Hence the f.p. curves have the form shown in Fig. 37. If a fused mixture is allowed to cool, the two free elements and the compound can be detected in the solidified product under the microscope. P. Fischer obtained zinc selenide by an electrolytic process. J. Margottet obtained zinc selenide by passing the vapour of hydrogen selenide over zinc at a red-heat; and when the amorphous yellow product is heated in a slow current of hydrogen, it forms yellowish-red cubical crystals. M. Grzenkowsky did not obtain the selenide free from metal by this means. H. Fonzes-Diacon obtained zinc selenide by the action of hydrogen selenide on the vapour of zinc chloride; and M. Grzenkowsky passed hydrogen selenide over the heated chloride and afterwards washed out the undecomposed chloride by warm water in which the selenide is insoluble. H. Fonzes-Diacon also obtained this selenide by reducing a mol of zinc selenate with 4 mols of carbon in an electric furnace; or by melting zinc selenate in an electric arc furnace. L. Moser and K. Atynsky obtained lemon-yellow zinc selenide, $ZnSe$, by the action of a zinc salt on hydrogen selenide out of contact with air. It decomposes on drying. P. Fischer made the selenide by electrolysis as in the case of copper selenide (*q.v.*).

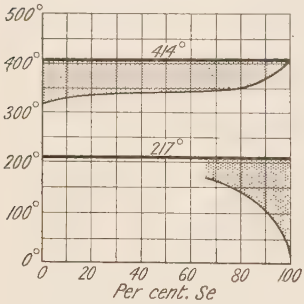


FIG. 37.—Freezing-point Curve of the Binary System: Zinc–Selenium.

According to I. Schindelmeiser, on adding 0·025 grm. of selenious acid to the flask of a Marsh's apparatus, the evolution of hydrogen practically ceased, the pieces of zinc being coated with a brown film and a flocculent, brown-red precipitate appearing in the acid soln. This precipitate was found to be a zinc selenide containing from 11 to 19 per cent. of zinc. When aluminium and sodium hydroxide soln. were employed, selenious acid also caused the evolution of hydrogen to cease after a time. In no case was a mirror obtained. Selenious acid and arsenious oxide were then introduced together into a Marsh's apparatus. So long as selenious acid remained in soln., no arsenical mirror formed, but when the selenium had separated as a precipitate, the arsenic came over, no trace remaining in the precipitate.

J. Margottet described the crystals as cubic, but H. Fonzes-Diacon said that they are hexagonal, without action on polarized light. W. P. Davey found that the X-radiogram corresponds with two interpenetrating face-centred cubes –calcium fluoride type—of side a=5·651 A., and a calculated density of 2·283 A.; and W. Zachariasen, a=5·661 A. L. Pauling, W. H. Rothery, and E. J. Guy discussed the spatial relations of the atoms. H. Fonzes-Diacon gave for the sp. gr., 5·42 at 15°. J. Margottet gave 3·4 for the sp. gr. at 15°; and F. A. Henglein gave 26·9 for the mol. vol. M. L. Huggins studied the atomic structure of the crystals. M. Grzenkowsky said that the sp. gr. is 5·27; and M. Chikashige and R. Kurosaura gave 5·29 at 21°; and added that it does not fuse below 1100°. C. Fabre gave for the heat of formation of the crystalline selenide $(\mathrm{Zn},\mathrm{Se}_{\mathrm{metal}})$=40·40 Cals.; for the crystalline precipitate, 34·0 Cals.; and for the amorphous precipitate, 33·6 Cals. When heated in oxygen, zinc selenite is first formed, and this decomposes into selenium dioxide and zinc oxide. According to J. J. Berzelius, the lemon-yellow, amorphous powder is decomposed by cold, dil. nitric acid, without the evolution of nitrous fumes; the zinc passes into soln. and the selenium remains. If the acid be heated, the selenium passes into soln. as selenious acid. H. Fonzes-Diacon said that fuming hydrochloric acid dissolves the selenide with the evolution of hydrogen selenide; hydrogen chloride gas is almost without action. Chlorine, and the vapours of bromine and iodine, displace the selenium. Precipitated zinc selenide is yellowish-white, and when dried over sulphuric acid in an atm. of hydrogen it is pale-yellow. It is quickly altered by exposure to air and is coloured red. Moist zinc selenide remains yellow if kept in darkness, but is quickly reddened in sunlight; well-dried selenide is very little altered by exposure to sunlight; the oxygen of the air, as well as moisture, also reddens the yellow selenide, and this is also the case with hydrogen dioxide. The red colour is due to the separation of selenium, which can be removed by washing with carbon disulphide. Hydrogen dioxide also converts zinc selenide into selenate.

M. Chikashige and R. Hikosaka observed that cadmium and selenium unite to form **cadmium selenide,** CdSe. The reaction between the elements begins to be appreciable at about 360°, and its velocity increases with rise of temp. The cadmium selenide does not dissolve in either of the molten elements, which are themselves practically immiscible. The f.p. curve had the form shown in Fig. 38. When, therefore, a mixture of the two elements is fused and cooled, the product consists of a mixture of cadmium selenide, cadmium, and selenium, which are readily recognized under the microscope. The proportion of the compound in the product depends on the temp. to which the mixture had been heated and on the length of the period of heating. M. Kröger studied the mechanism of the reaction lattices between the vapours of cadmium, Cd, and selenium, Se_6. G. Little said that selenium vapour unites with heated cadmium with incandescence, forming cadmium selenide. J. Margottet obtained the selenide by heating cadmium in a current of hydrogen selenide, and subliming the product in hydrogen at a dull red-heat. P. Fischer obtained the selenide by an electrolytic process. M. Grzenkowsky found that the selenide obtained by passing hydrogen selenide over heated cadmium is always contaminated with some metal, and he obtained better results by passing the gas over the heated chloride and afterwards washing out the undecomposed chloride with warm water, which does not attack cadmium selenide. H. Fonzes-Diacon also heated cadmium chloride in a current

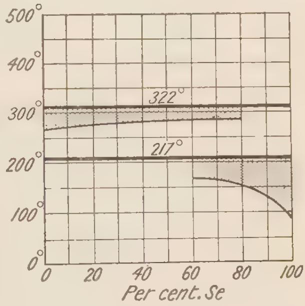


Fig. 38.—Freezing-point Curve of the Binary System: Cadmium–Selenium.

of hydrogen selenide dil. with hydrogen. H. Uelsmann, and C. Fabre prepared dark brown selenide by the action of hydrogen selenide on a soln. of cadmium chloride, sulphate, or nitrate. L. Moser and K. Atynsky made dark brown cadmium selenide as in the case of the zinc selenide. E. Reeb stated that hydrogen selenide acts on soln. of cadmium salts very much like hydrogen sulphide. G. Little converted the yellow sulphide into dark grey, tabular crystals by fusion with borax. J. Margottet's sublimed product appeared in black, prismatic crystals. The colour may be pale brown, yellow, or blood-red. W. Zachariasen gave for the hexagonal lattice $a=4\cdot30$ A., and $a:c=1:1\cdot630$; and the calculated density 5·63. M. L. Huggins studied the atomic structure of the crystals. G. Little said that the sp. gr. is 5·787; J. Margottet, 5·80; H. Fonzes-Diacon, 5·81 at 15°; M. Chikashige and R. Hikosaka, 5·81 at 16°; and M. Grzenkowsky, 5·61. M. Chikashige and R. Hikosaka said that cadmium selenide is infusible below 1350°. C. Fabre gave 26 Cals. for the heat of formation of the crystalline selenide, and 22·9 Cals. for the precipitated. Cadmium selenide behaves very like zinc selenide (*q.v.*). Acids quickly decompose cadmium selenide, but chlorine requires an elevated temp.; with oxygen it forms cadmium oxide and selenium dioxide. E. Reeb found that the precipitated selenide behaves very like the precipitated sulphide.

It is doubtful if **mercurous selenide,** Hg_2Se, has been prepared. G. Little[5] reported it to be formed in purple or violet, cubic crystals, of sp. gr. 8·877, by sublimation from a mixture of mercury and selenium, but H. Uelsmann showed that this product is probably impure mercuric selenide. G. Pellini and R. Sacerdoti also failed to confirm the existence of mercurous selenide. H. Fonzes-Diacon obtained impure mercurous selenide by the action of hydrogen selenide on mercurous chloride, but if mercurous acetate be suspended in water, acidified with acetic acid, hydrogen selenide converts it into a black powder of mercurous selenide. L. Moser and K. Atynsky obtained a mixture of mercuric selenide and selenium by the action of a mercurous salt on a soln. of hydrogen selenide out of contact with air. According to J. J. Berzelius, when selenium and mercury are heated together, combination occurs without the emission of light. If an excess of mercury be present, the distillation of the mercury from the mixture leaves a solid, tin-white, selenide—according to H. Uelsmann, J. Margottet, H. Fonzes-Diacon, and G. Pellini and R. Sacerdoti, **mercuric selenide,** HgSe—which, at a high temp., sublimes, without fusion, in laminæ with a metallic lustre. On the other hand, if selenium be in excess, a portion of that element first sublimes; this is followed by a grey sublimation which is less distinctly crystalline and finally the tin-white selenide sublimes. J. Margottet said that combination of vitreous selenium and mercury occurs at ordinary temp. G. Pellini and R. Sacerdoti found that at ordinary press., the combination of mercury and selenium, under the action of heat, takes place slowly, and that an excess of selenium is necessary for the preparation of mercuric selenide, HgSe. The excess of selenium can be separated from the crystalline selenide by slow fractional distillation. If the two elements are mixed in at. proportions, complete combination occurs only in a sealed tube, when heated to 350°–600° for some time. The viscid amalgams obtained by triturating mercury and selenium in a mortar consist of mixtures of mercury and mercuric selenide. Mixtures of the two elements containing 70 to 98 at. per cent. of selenium undergo partial fusion, and there is an arrest in the cooling curves at 132°–139°; while the heating curves show an arrest at 216°–218° when the m.p. of selenium is 220°. Mercuric selenide dissolves very sparingly in selenium even at a high temp.; the arrest in the heating curves at 216°–218° corresponds with the eutectic Se+HgSe; while the arrest at 132°–134° in the cooling curves corresponds with the rapid transformation of surfused selenium into the stable, metallic form. M. Grzenkowsky found that when hydrogen selenide is passed over heated mercury, the resulting selenide can be freed from mercury by heating the product in a current of hydrogen. H. Fonzes-Diacon obtained cubic crystals of mercuric selenide by the action of hydrogen selenide on the vapour of mercuric chloride. H. Uelsmann obtained mercuric selenide by passing hydrogen selenide into a soln. of mercuric chloride. At first *mercuric selenochloride*, HgSeCl, is precipitated, but this soon passes into the selenide. L. Moser and K. Atynsky obtained black mercuric selenide in an analogous way.

H. Rose found at Tilkerode, Harz, a mineral which he regarded as a mixture of lead and mercury selenides, and which C. M. Marx found to be a compound of selenium and mercury. C. F. Naumann called it **tiemannite**—after W. Tiemann. Occurrences in other parts of the Harz were described by W. J. Jordan, C. F. Rammelsberg, G. Frebold, H. Rose, W. Geilmann and H. Rose, and B. Kerl; in California, by J. D. Dana, I. Domeyko, and G. F. Becker; in Utah, by G. J. Brush, and S. L. Penfield; and in the Sierra de Umango, Argentine, by F. Klockmann. The best representative value of the analyses, reported by B. Kerl, T. Petersen, C. F. Rammelsberg, S. L. Penfield, and F. Klockmann, is HgSe, although C. F. Rammelsberg gave Hg_6Se_5, which he was inclined to regard as a mixture of mercuric and mercurous selenides, $4HgSe+Hg_2Se$. W. Geilmann and H. Rose observed that tiemannite grows as a solid crust on clausthalite in contact with mercuric chloride at 300°. The mineral commonly occurs in steel-grey or dark lead-grey compact or granular masses; it also occurs in cubic crystals, usually tetrahedral in habit, and exhibiting twinning about a trigonal axis. There is no cleavage, according to F. Fouqué and A. Michel-Lévy. The violet or purple, cubic crystals obtained artificially by G. Little, and the steel-grey, octahedral crystals by H. Uelsmann, and J. Margottet, have not been definitely identified with tiemannite. W. F. de Jong found that the X-radiogram indicates a space-lattice like sphalerite with side a=8·41 A.; and the distance between the selenium and mercury atoms, 2·62 A. W. Hartwig's X-radiogram corresponds with a space-lattice of the zincblende type. W. Zachariasen gave for the four-centred cubic lattice a=6·068 A. M. L. Huggins studied the atomic structure of the crystals. B. Kerl gave 7·10 to 7·37 for the sp. gr. of the mineral; T. Petersen gave 7·15; and S. L. Penfield, 8·305 to 8·473. The lower values probably apply to impure specimens. J. Margottet found 8·165 to 8·21 for the sp. gr. of the artificial selenide; H. Fonzes-Diacon, 8·207 at 15°; and M. Grzenkowsky, 7·78. F. A. Henglein gave 34·1 for the mol. vol. The hardness of the mineral is about 2·5. H. Fonzes-Diacon found that when mercuric selenide is heated in a closed tube, it sublimes without melting, while mercurous selenide gives a sublimate of mercuric selenide and mercury droplets. C. Fabre found that the heat of formation of the crystalline selenide from its elements is 19·70 Cals., and for the precipitated selenide, 16·00 Cals. F. Beijerinck, and R. G. Harvey said that the mineral is a good conductor of electricity. E. T. Wherry found tiemannite to be a fair radio-detector.

According to H. Pélabon, mercury selenide is attacked by hydrogen at temp. above 400° with the production of hydrogen selenide and mercury, the reaction being limited by the inverse action of hydrogen selenide on mercury. The proportion of hydrogen selenide found in the gaseous products of the reaction increases with the temp. and with a diminution of the initial press. Thus, at 540° with an initial press. of 760 mm. equilibrium is attained when 15 per cent. of hydrogen selenide is present, whilst at 440° only 0·52 per cent. is formed. On the other hand, with initial press. of about 380 mm. and 190 mm. at 540°, the percentages of hydrogen selenide formed become 19 and 27 respectively. When heated in dry oxygen mercuric selenide gives a sublimate of selenium dioxide, and this is followed by brown vapours which condense to mercurous selenite; mercurous selenide also forms selenite when heated in oxygen. Hydrogen dioxide converts mercuric selenide into selenate and selenic acid. Conc., boiling hydrochloric acid does not attack mercuric selenide, and if heated in hydrogen chloride, the mercuric selenide sublimes. Boiling sulphuric acid gives sulphur dioxide, forming mercury sulphate, and a green liquid containing free selenium. J. J. Berzelius found that mercuric selenide readily dissolves in cold aqua regia, forming mercuric selenite, while continued boiling with nitric acid converts it into mercurous selenite. H. Fonzes-Diacon found that mercurous selenide is easily attacked by conc. nitric acid, but the attack soon ceases because of the formation of a protective film of mercurous selenite. E. Reeb said that in many of its properties mercuric selenide behaves like mercuric sulphide.

H. Rose said that mercuric sulphide and selenide are isomorphous and are miscible, as solid soln., in all proportions. The isomorphous mixture is represented by a mineral described by C. M. Kersten, and H. Rose as a *selenschwefelquecksilber*. A. Breithaupt called it *mercury glance;* and W. Haindinger, **onofrite,** in reference to the fact that it was first obtained from San Onofre, Mexico. This may be the sulphoselenide of mercury described by A. M. del Rio in 1828, to which allusion has been made in connection with the occurrence of selenium. Occurrences also have been reported in Marysville, Utah, by G. J. Brush, J. S. Newberry, and S. L. Penfield; and in Kwei-Chau, China, by P. Termier. Analyses detailed by H. Rose, S. L. Penfield, G. J. Brush, and P. Termier, indicate that the mineral may be a **mercuric sulphoselenide,** $HgSe.HgS$, associated with more or less mercuric sulphide —say, $HgSe.HgS+3HgS$—or else, as S. L. Penfield regarded it, an isomorphous mixture of mercuric sulphide and selenide, $Hg(S,Se)$. It occurs compact, and granular, and of a greyish-black colour. W. Hartwig found that the space-lattice is of the zinc-blende type. The sp. gr. given by G. J. Brush ranges from 7·61 to 7·63; and by S. L. Penfield, 7·98 to 8·09. The hardness is 2·5. E. T. Wherry found the mineral to be a poor radio-detector. The mineral is not attacked by hot or cold nitric acid; but it is decomposed by aqua regia, and by chlorine.

A mineral from Guadalcazar, Mexico, was described by A. del Castillo and H. J. Burkart, and named by M. Adam, *guadalcazite*, and by T. Petersen as **guadalcazarite**. Its composition approaches closely to that of metacinnabarite; analyses reported by T. Petersen, and C. F. Rammelsberg indicate 14·01–14·58 per cent. sulphur; up to 1·08, selenium; 79·73–83·90, mercury; and 2·09 to 4·23, zinc. Its sp. gr. is 6·69 to 7·165, and its hardness 2·5. A. d'Achiardi reported a mineral from the mercury mines of Levigliani, Seravezza, Apaun Alps, Italy, and named it **leviglianite**. It is considered to be a ferruginous variety of quadalcazarite. W. Hartwig found that the space-lattice is of the zinc-blende type. T. W. Case found that its high resistance is not affected appreciably by light.

H. Uelsmann[6] prepared **mercuric oxydiselenide,** $HgO.2HgSe$, by boiling dichlorodiselenide with soda-lye. When heated it forms a sublimate of mercurous selenide and mercury. It readily dissolves in aqua regia. J. J. Berzelius obtained a glass spiess by fusing together a mixture of antimony trioxide and triselenide, assumed, without justification, to be *antimony oxyselenide*. H. Fonzes-Diacon prepared a *manganese oxyselenide* by heating manganese selenate to redness in a current of hydrogen. The greenish product develops hydrogen selenide when treated with hydrochloric acid; and when heated in air, it burns to manganese and selenium oxides. He also obtained *cobalt oxyselenide* in a similar way; and likewise also with *nickel oxyselenide*. These oxyselenides may be only mixtures.

H. Moissan[7] observed that at 610° boron combines energetically with selenium to form a selenide. P. Sabatier prepared **boron triselenide,** or *selenium boride*, B_2Se_3, by passing a slow, regular current of dry hydrogen selenide over boron, maintained at a bright-red heat, in a hard glass tube. The brownish-black boron is transformed into the yellowish-grey boron selenide without fusion, a little of the compound only being deposited in a pulverulent state on the tube beyond the boat. The selenide is much less fusible and volatile than the corresponding sulphide. Water acts violently on the grey boron selenide, disengaging hydrogen selenide, and at the same time liberating some red, pulverulent selenium; hence, doubtless, the disgusting odour of the substance is due to the action of atm. moisture. The yellow, pulverulent selenide deposited beyond the boat is decomposed by water without deposition of selenium; hence its composition is doubtless comparable with that of the sulphide, and would be represented by B_2Se. This formula agrees with the analyses. If the residue obtained in the preparation of the triselenide be treated with water, the brown residue which remains may be a subselenide—possibly *boron tetritaselenide*, B_4Se—but it has not been carefully examined. J. Hoffmann observed that boron is a product of the action of selenium on iron boride or ferroboron, and on manganese boride, as well as of hydrogen selenide on iron boride.

J. J. Berzelius[8] found that an aq. soln. of potassium polyselenide gives a flesh-coloured precipitate with soln. of aluminium salts. The product loses selenium at a red-heat. It was probably a mixture of selenium and aluminium selenide. According to F. Wöhler, aluminium at a red-heat unites with selenium with incandescence, forming a black powder which, by pressure, acquires a dark, metallic lustre; emits an odour of hydrogen selenide when exposed to air; and rapidly evolves that gas, with the separation of selenium, when treated with water. H. Fonzes-Diacon ignited an intimate mixture of selenium and fine aluminium powder by means of a burning magnesium ribbon. The combustion is propagated throughout the mass, and a yellowish-grey fibrous mass of **aluminium selenide,** Al_2Se_3, is obtained below a black layer of impure selenide. It evolves hydrogen when treated with water. These results were confirmed by C. Matignon. D. M. Liddell obtained the selenide by dropping selenium into molten aluminium. L. Moser and E. Doctor prepared the selenide Al_2Se_3, by passing the vapour of selenium over aluminium heated in vacuo, and also by H. Fonzes-Diacon's process. The light brown powder so formed was unstable in air. L. Moser and K. Atynsky said that J. J. Berzelius' statement that hydrogen selenide gives a dark red aluminium selenide when passed into a soln. of an aluminium salt is not correct; they could not make the selenide by the action of an aluminium salt in a soln. of hydrogen selenide. M. Chikashige and T. Aoki examined the f.p. of mixtures of the two elements, and the results are summarized in Fig. 39. The maximum at 953° corresponds with the formation of **aluminium tetratritaselenide,** Al_3Se_4. The formation of this compound by heating the two elements together is frequently accompanied by an explosion unless the mixture contains more than 90 per cent. of selenium. The compound crystallizes out from all fused mixtures of the two elements, and in accordance with this, the two branches of the compound curve on the f.p. diagram cover the whole of the region from pure aluminium to pure selenium. The eutectics are therefore very nearly coincident with the f.p. of the two elements. Aluminium selenide decomposes in contact with moist air with the formation of hydrogen selenide and aluminium hydroxide. H. Fonzes-Diacon gave 3·437 for the sp. gr. of aluminium selenide, Al_2Se_3, at 15°. Hydrogen was without action at a white-heat; if heated in oxygen, a superficial film of alumina is formed; the selenide is quickly attacked by humid air, giving off hydrogen selenide; with water freed from air, torrents of hydrogen selenide are given off; chlorine transforms the heated selenide into selenium and aluminium chlorides; hydrochloric acid rapidly attacks it with the evolution of hydrogen selenide; dil. sulphuric acid acts similarly; and when mixed with carbon it can be heated in an electric arc *sans être sensiblement decomposé*. G. Natta studied the action of aluminium selenide on alcohols and ethers.

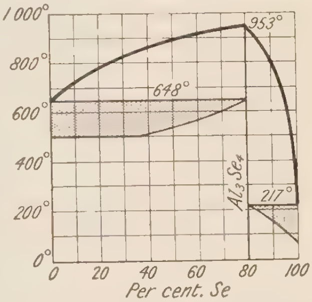


Fig. 39.—Freezing-point Curve of Aluminium and Selenium.

C. Renz[9] found that an **indium selenide** can be formed as a black brittle mass, by the direct union of the elements. According to W. Crookes, A. Lamy, and E. Carstanjen, a gram-atom of selenium unites with two gram-atoms of thallium when the elements are melted together, and the reaction is not attended by incandescence. T. Murakami, however, did obtain the triselenide in two forms. His observations on the f.p. of the system are summarized in Fig. 40. There are three compounds, of which two present themselves as maxima on the f.p. curve, whilst the third decomposes below its m.p. There are three eutectic points, at 281°, 283°, and 150° respectively. These correspond with alloys containing 1 per cent., 21 per cent., and 52 per cent. of selenium respectively. The monoselenide melts at 368°, and TlSe at 310°. The triselenide decomposes at 265°, and undergoes a transformation at 165°. There are two gaps of miscibility in the liquid state, extending from 4 to 14·5 per cent. Se, and from 55 to 97·5 per cent. All the compounds are brittle. H. Pélabon found that mixtures with over 50 per cent. of selenium solidify between 178° and 195°, one of the liquid phases being the pentaselenide and the other a soln. of this in selenium. The m.p. curve has a eutectic at 315° corresponding with 42·9 at. per cent. of selenium. The curve then rises to a maximum at 332° representing the **thallosic selenide,** TlSe, that is, $Tl_2Se.Tl_2Se_3$, and finally falls to 195°, the m.p. of **thallium pentaselenide,** Tl_2Se_5. There is no break corresponding with **thallium triselenide,** Tl_2Se_3; nor could E. Carstanjen prepare the trisulphide. L. Rolla measured the variation in the surface tension of the alloys and observed evidence of only Tl_2Se and TlSe, but not of Tl_2Se_5 or Tl_2Se_3. F. Kuhlmann obtained **thallous selenide,** Tl_2Se, in dark grey plates, by the action of hydrogen selenide on a soln. of thallous carbonate. L. Moser and K. Atynsky obtained bluish-black thallous selenide in a similar way. The product obtained by the fusion process is dark grey or black, hard, brittle mass with a conchoidal, not a crystalline, fracture. The metallic lustre soon tarnishes on exposure to air. F. Kuhlmann gave 340°, and H. Pélabon, 338° for the m.p. F. Kuhlmann added that there is a large contraction when the molten selenide freezes. C. Fabre gave 17·72 Cals. for the heat of formation of the crystalline selenide, and 14·72 Cals. for the precipitated. H. Pélabon measured the electrical resistance of Tl_2Se. E. Carstanjen found that thallous selenide is scarcely attacked by cold, dil. sulphuric acid, but when heated hydrogen selenide is slowly evolved. F. Kuhlmann found that the precipitated selenide furnishes hydrogen sulphide when treated with sulphuric or hydrochloric acid; and with nitric acid, it forms thallous selenite. E. Carstanjen obtained thallosic selenide by fusing two gram-atoms of thallium with more than one gram-atom and less than three gram-atoms of selenium. The liquid solidifies to a black crystalline mass, which is not attacked by cold, conc., or by boiling, dil. sulphuric acid; but hot, conc. sulphuric acid yields sulphuric dioxide, a red deposit of selenium, and a green liquid. A. E. Nordenskjöld reported a leaden grey, compact, and brittle mineral from a mine at Skrikerum, Sweden, and he named it **crookesite**—after W. Crookes. Its composition approximates copper, silver, thallium selenide, $(Cu,Ag,Tl)_2Se$. Its sp. gr. is 6·90, and its hardness is 2·5 to 3·0. T. W. Case found that its high resistance is not appreciably affected by light.

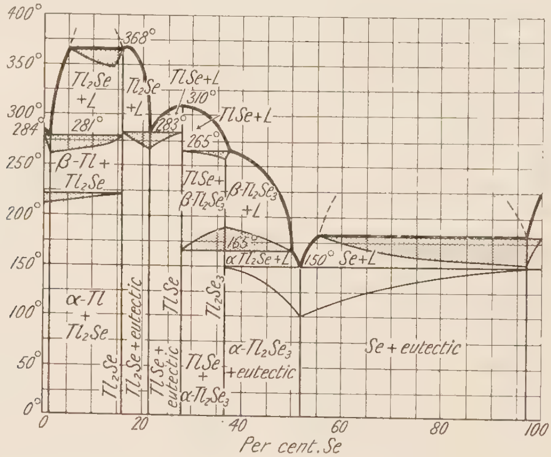
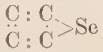


FIG. 40.—Melting-point Curve of the Binary System: Selenium–Thallium.

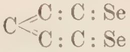
J. J. Berzelius found that when aq. soln. of cerous salts are treated with an alkali selenide, a pale red precipitate, probably of impure *hydrated cerous selenide*, is formed. It becomes darker in colour on exposure to air. If cerous selenite be heated in a current of hydrogen, **cerous selenide** is formed. If some ceric oxide be present, a portion of the selenium passes off with the hydrogen. The brown powder is unstable giving off hydrogen selenide. When heated in air, a sublimate of selenium dioxide is formed, and leaves behind a white basic ceric selenite. When the selenide is treated with the weakest of the acids, hydrogen selenide is formed, but water itself has no action.

According to A. von Bartal,[10] on distilling a mixture of 1 mol of carbon tetrabromide with 2 mols of amorphous red selenium, a small quantity of a reddish-yellow oil passes over between 160° and 190°; the fraction distilling about 190° sets to a red solid on cooling. The residue, after extraction alternately with carbon disulphide, phenol, alcohol, and ether, yields a greyish-black powder having the composition $C_9Br_2Se_4$; it decomposes at high temp. and dissolves in conc. sulphuric acid to a reddish-brown soln. Heated with very conc. sodium hydroxide it gives **carbon tetritaselenide,** C_4Se, as a black amorphous powder which is sparingly soluble in hot, conc. sulphuric acid, forming a pale brown soln. It is infusible, and decomposes when heated, glowing in air, and leaves no residue. It is difficult to prepare free from bromine. If hydrochloric acid be added to the soln. of $C_9Br_2Se_4$ in soda-lye, a dark violet-brown powder of **carbon pentitadiselenide,** C_5Se_2, is precipitated. These two selenides are supposed to be constituted:



$$\begin{matrix} C:C \\ \ddot{C}:\dot{C} \end{matrix}\!\!>\!Se$$

Carbon tetritaselenide, C_4Se



$$C\!\!<\!\!\begin{matrix} C:C:Se \\ C:C:Se \end{matrix}$$

Carbon pentitadiselenide, C_5Se_2

The pentitadiselenide has a conchoidal fracture. It neither fuses nor sublimes; but when heated in air it glows and burns, leaving only a trace of residue which probably represents contamination with a sodium salt. Hot conc. sulphuric acid forms a reddish-brown soln.; it also forms a reddish-brown soln. with soda-lye, and is again precipitated by neutralizing the liquid with hydrochloric acid.

In 1869, B. Rathke prepared **carbon diselenide,** CSe_2, by the action of moist vapour of carbon tetrachloride on phosphorus pentaselenide; the stream first forms hydrogen selenide, which then reacts: $CCl_4+2H_2Se=CSe_2+4HCl$. The compound is not obtained by the action of the vapour of selenium dioxide on red-hot carbon, by melting a mixture of potassium ferrocyanide with an excess of selenium, or by heating a mixture of phosphorus selenide, water, and carbon tetrachloride in a sealed tube. Neither A. Stock and E. Willfroth nor H. V. A. Briscoe and co-workers were able to prepare carbon diselenide by the action of selenium vapour on carbon at 1000°, but a partial replacement may occur—*vide infra*, carbon sulphoselenide. A. von Bartal's attempt to prepare carbon diselenide by passing carbon tetrachloride vapour over cadmium selenide, heated to a dull red-heat, resulted in the formation of a mixture of hexachloroethane, selenium chloride, selenium, and a trace of carbon diselenide. Carbon diselenide, said B. Rathke, is a greenish-yellow liquid which smells not unlike carbon disulphide. The carbon diselenide boils near 90°. A soln. of carbon diselenide when boiled with potash-lye forms a dark brown soln. of potassium selenide; with alcoholic soln. of potassium hydroxide, a deep red soln.; and with a conc. soln. of potassium hydroxide in alcohol, yellow needles of **potassium selenoxanthate** are formed. B. Rathke said that the characteristic radish-like odour of selenium when heated in charcoal in the blowpipe is due to carbon diselenide and not to a suboxideof selenium.

If a soln. of selenium dioxide be treated with calcium silicide and a little hydrochloric be added, a vermilion *selenosilicon*, analogous to F. Wöhler's[11] sulphosilicon—**6**. 40, 60—is obtained. It smells of hydrogen selenide, and with ammonia gives off hydrogen. When heated it gives off selenium and hydrogen selenide. According to P. Sabatier, when crystalline silicon is heated to redness—below the b.p. of selenium—in a current of dry hydrogen selenide, it is converted into **silicon diselenide,** $SiSe_2$, without incandescence. After fusion, the diselenide is a hard, lustrous mass, of semi-metallic appearance. Under ordinary conditions, silicon selenide evolves a very irritating odour, due, doubtless, to the hydrogen selenide formed by the action of the moisture in the atm. At a red-heat in a current of air, or dry oxygen, the selenide is converted into silica, selenious anhydride, and selenium. Cold water decomposes it with evolution of hydrogen selenide and separation of silica, but after a time decomposition slackens, and, although it is accelerated on warming, the silicon selenide is never completely decomposed, probably because it is protected by the silica that separates. With potassium hydroxide soln., which dissolves both the hydrogen selenide and the silica, decomposition becomes complete after some time. Aqua regia acts gradually on the selenide with separation of hydrated silica. A. E. van Arkel and J. H. de Boer made **titanium selenide** by passing the vapour of the metal chloride and selenium over a heated tungsten filament; I. Oftedal also made the selenide, $TiSe_2$, by heating an intimate mixture of the elements. The tabular, red, hexagonal crystals have an X-radiogram corresponding with a hexagonal lattice with $a=5{\cdot}995$A., $c=3{\cdot}533$A., and $a:c=1:1{\cdot}697$. The calculated density is 5·29. The crystals are similar to those of cadmium iodide, stannic sulphide, and titanium sulphide and telluride. G. Natta, and V. M. Goldschmidt studied the structure of the crystals. A. E. van Arkel and J. H. de Boer similarly prepared **zirconium selenide,** $ZrSe_2$, and **hafnium selenide**, $HfSe_2$. According to A. E. van Arkel, zirconium selenide crystallizes in the trigonal system and has the axial ratio $a:c=1:1{\cdot}63$, and the edge of the hexagon is 3·79 A., and there is one mol in a unit cell. G. Natta and V. M. Goldschmidt made some observations on this subject. H. Moissan and H. Martinsen[12] prepared a **thorium selenide** by the action of the selenium vapour, mixed with hydrogen, on thorium tetrachloride or tetrabromide; or, according to H. Moissan and A. Étard, on thorium carbide. The black mass gives off hydrogen selenide when treated with acids. A. E. van Arkel and J. H. de Boer made thorium selenide by the process used for titanium selenide.

According to J. J. Berzelius,[13] tin unites directly with selenium when a mixture of the two elements is heated; and the combination is attended by incandescence. H. Pèlabon found that the f.p. of mixtures of tin with increasing proportions of selenium rises first rapidly, then more gradually, to the maximum point 860° and 640°, the two f.p. of the mixture corresponding with *sesquiselenide*, Sn_2Se_3; after that the curve falls very gradually to 550°, the f.p. of the mixture containing 30 gram-atoms of selenium to one of tin, and shows no peculiarity for the diselenide, $SnSe_2$. W. Biltz and W. Mecklenburg's results are illustrated in Fig. 41. The maximum at 861° corresponds with the formation of the monoselenide; and the break near 650° corresponds with either the sesquisulphide or the disulphide. The two eutectics consist of almost pure tin and selenium respectively.

J. J. Berzelius, and H. Uelsmann prepared **stannous selenide** or **tin monoselenide,** SnSe, by direct fusion of a mixture of the elements. The conditions of equilibrium are indicated in Fig. 41. A. Ditte melted the mixture of elements in a porcelain boat in a current of hydrogen, and found that the molten mass begins to distil at a bright red-heat, forming a green vapour. The distillation readily proceeds at a white-heat, and crystals of the monoselenide collect in the cooler part of the tube. R. Schneider obtained the selenide by adding powdered selenium to molten, anhydrous stannous chloride, and heating the mixture until the liquid is clear. Some stannic chloride volatilizes, and on cooling, crystals of the monoselenide remain. These are freed from stannous chloride by washing with dil. hydrochloric acid. L. Moser and K. Atynsky obtained it by the action of a stannous salt on a soln. of hydrogen selenide out of contact with air. Ordinary stannous selenide can be purified by recrystallization from molten stannous chloride. H. Uelsmann precipitated dark brown or black stannous selenide by passing a current of hydrogen selenide into a soln. of

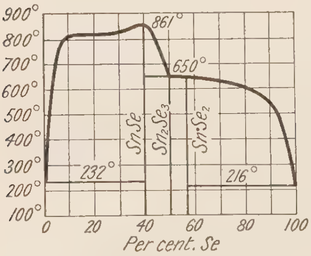


FIG. 41.—Freezing-point Curve of Mixtures of Tin and Selenium.

stannous chloride. The fused selenide is a steel-grey, crystalline mass; and that crystallized from stannous chloride appears in steel-grey prisms or plates, which, according to R. Schneider, are probably isomorphous with stannous sulphide, and their sp. gr. is 5·24 at 15°; A. Ditte said that the sublimed selenide has a sp. gr. of 6·179 at 0°. H. Pélabon gave 860° for the m.p., and W. Biltz and W. Mecklenburg, 861°. H. Pélabon studied the thermoelectric force of platinum coupled with tin-selenium alloys of different composition. The form of the curves varies with the temp., but all show an angular point corresponding with the selenide SnSe. The selenide $SnSe_2$ is not indicated by any particular change in direction of the curve. At the hot juncture the current passes from platinum to the alloy for Pt-SnSe, and from the alloy to platinum for Pt-$SnSe_2$. A couple formed by platinum and an alloy of composition intermediate between that of the two selenides, and varying slightly with the temp., will have no thermoelectric force. According to A. Ditte, the monoselenide may be volatilized unchanged in an atm. of hydrogen, but at a white-heat a little hydrogen selenide is formed. W. Herz gave 1133×10^{12} for the vibration frequency of SnSe. J. J. Berzelius found that when heated in air, without fusion, selenium is volatilized and stannic oxide remains. The monoselenide is insoluble in water; and, according to R. Schneider, it is oxidized by a carbon disulphide soln. of iodine, or by heating it with iodine, forming stannic selenide and iodide; bromine acts in an analogous manner. A. Ditte said that stannous selenide behaves very like stannous sulphide towards hydrogen chloride; at ordinary temp. there is no action; at a red-heat, stannous chloride and selenium, with a little hydrogen selenide, are volatilized. At ordinary temp., crystalline stannous selenide is not attacked by hydrochloric acid, but it is slowly attacked by the boiling acid, and a state of equilibrium ensues as in the case of stannous sulphide. Hot, conc. nitric acid slowly oxidizes stannous selenide, forming selenium and tin dioxides; it is easily dissolved by aqua regia. Precipitated stannous selenide is easily attacked by alkali-lye, but the boiling lye has very little action on the crystallized selenide; both forms readily dissolve in soln. of alkali sulphides or selenides to form sulpho- for selenostannates.

R. Schneider said that **stannic selenide,** or **tin diselenide,** $SnSe_2$, cannot be prepared by a method analogous to that used for making muscovite gold; but G. Little obtained it by passing the vapour of selenium over heated tin. The conditions under which the diselenide can be obtained from its elements are indicated in Fig. 41. According to R. Schneider, 5 parts of iodine are triturated with 8 to 10 parts of stannic iodide, and then with stannous selenide, and finally with enough carbon disulphide to make a mushy mass; the carbon disulphide extracts the stannic iodide, leaving stannic selenide as a residue. J. J. Berzelius treated a soln. of stannic chloride with hydrogen selenide, and obtained stannic selenide as a dark yellowish-red or reddish-brown precipitate; L. Moser and K. Atynsky used an analogous process; and A. Ditte, by treating a soln. of an alkali selenostannate or sulphoselenostannate with hydrochloric acid. The fused diselenide appears as a tin-white or dark brown mass with a conchoidal fracture. V. M. Goldschmidt studied the structure of the crystals. G. Little gave 5·133 for the sp. gr., and R. Schneider, 4·85. W. Biltz and W. Mecklenburg gave 650° for the m.p. H. Pélabon's observations on the thermoelectric properties have been discussed in connecton with the monoselenide. H. Uelsmann found that when the diselenide is heated in hydrogen it forms the monoselenide. The diselenide, said R. Schneider, is not attacked by water or by dil. acids, and G. Little, not by hydrochloric acid, but R. Schneider said that it is attacked by the boiling acid. When melted with iodine, or treated with a soln. of iodine in carbon disulphide, selenium and stannic iodide are formed: $SnSe_2+2I_2=2Se+SnI_4$; bromine acts in an analogous way. Tin diselenide is decomposed by nitric acid; and is readily dissolved by aqua regia, particularly if warm. conc. sulphuric acid dissolves the diselenide, forming an olive-green soln. which gives a precipitate of selenium when poured into water, while stannic sulphate remains in soln. The diselenide is dissolved by aq. ammonia, or by alkali-lye, particularly if warm; forming a blood-red soln. from which hydrochloric acid precipitates dark red tin diselenide. H. Uelsmann found that precipitated stannic selenide forms a blood-red soln. with alkali-sulphides, and the soln., when exposed to air, soon deposits selenium. According to A. Ditte, when stannic selenide is dissolved in a soln. of potassium selenide, and the clear liquid evaporated in vacuo, crystals of **potassium selenostannate,** $K_2SnSe_3.3H_2O$, are formed; they rapidly change when exposed to air; similarly with **sodium selenostannate,** $Na_2SnSe_3.nH_2O$. These compounds have properties resembling those of thiostannates.

According to J. J. Berzelius,[14] lead and selenium unite when heated, with the evolution of light and heat, forming a grey, porous mass which becomes silver-white when burnished. A small proportion of selenium united with lead renders it whiter, less ductile, and more fusible. K. Friedrich and A. Leroux were able to determine only a single branch of the f.p. curve of selenium and lead. The eutectic lies close to the lead end; and there is a maximum at 1065° corresponding with **lead selenide,** PbSe. According to H. Pélabon, lead combines directly with selenium, and the product forms homogeneous mixtures with an excess of either constituent. Lead alone commences to solidify at 325°; at 745°, if 2 per cent. of selenium is present, and at 800°, if 4·5 per cent. is present. In these cases, the completion of the solidification occurs at 325°. With increasing proportions of selenium the f.p. rises until it reaches a maximum at 1065°, with 27·62 per cent. of selenium. This corresponds with lead selenide. Mixtures with less selenium are therefore mixtures of lead and lead selenide. As the amount of selenium increases beyond 27 per cent., the f.p. falls rapidly to 673°, and there remains constant for mixtures containing 45 to nearly 100 per cent. of selenium. Mixtures containing over 45 per cent. of selenium separate into two layers: the upper layer is selenium alone, the lower one, solidifying at 673°, is a soln. of selenium in lead selenide, and not *lead diselenide*, $PbSe_2$, because (i) when allowed to solidify in a vacuum it rapidly loses selenium; (ii) on heating it loses selenium, without melting, until PbSe remains; (iii) selenium can be removed by washing with hot conc. potassium cyanide soln. The lower layer of the liquid just indicated solidifies to a greyish-black solid with a lamellaceous fracture. Mixtures containing 27 to 45 per cent. of selenium are solns. of lead selenide and selenium. Fig. 42 is compiled from both sets of observations.

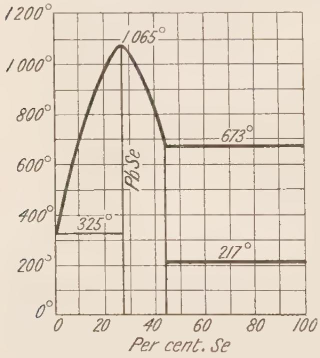


FIG. 42.—Freezing-point Curve of Alloys of Lead and Selenium.

J. Margottet, and G. Little prepared lead selenide by heating a mixture of the two elements, above the m.p. of lead. The mixture begins to spit at a dull red-heat, combination occurs, and the mixture solidifies. F. Rössler melted an intimate mixture of 50 grms. of lead and one gram of selenium under borax, and allowed it to cool slowly. The cubic crystals are separated from the matrix by using the product as anode in the electrolysis of a soln. of 50 grms. of lead and sodium acetates in 600 c.c. of water and 10 c.c. of acetic acid, and a current density of 2–3 amp. per sq. dm. A. C. Vournasos melted a mixture of the two elements under paraffin. H. Fonzes-Diacon reduced lead selenate to selenide by means of hydrogen at a white-heat, also by means of 4 times its wt. of carbon in an electric furnace; he also obtained it by the action of hydrogen selenide, mixed with nitrogen, on lead chloride at a red-heat; and by heating lead selenochloride with hydrogen, boiling water, or conc. soln. of potassium hydroxide or sodium thiosulphate. J. J. Berzelius also obtained the selenide by the action of hydrogen selenide on a soln. of a lead salt; and L. Moser and K. Atynsky obtained the black selenide in an analogous way. J. Brooks obtained the hydrosol by the action of hydrogen selenide on a soln. of lead acetate and gelatin.

In 1805, J. C. L. Zincken examined a mineral from Zorge, Harz, before selenium was discovered, and it seems to have been regarded as a cobaltiferous galena, for J. F. L. Hausmann called it *Kobaltbleierz*. It was not until 1824 that F. Stromeyer and J. F. L. Hausmann showed that the mineral is a lead selenide, and they called it *Selenblei*, and when cobalt was present, H. Rose called the mineral *Selenblei mit Selenkobalt*, and J. C. L. Zincken, *Selenkobaltblei*. F. S. Beudant named it *clausthalie*, in allusion to its occurrence at *Clausthal*, and J. D. Dana altered this to **clausthalite.** W. Haidinger suggested calling the variety containing cobalt, *tilkerodite*, from Tilkerode, where it occurs, and E. F. Glocker included both minerals in the general term *Selenbleiglanz*, but the name clausthalite has taken its place. Occurrences in the Harz were described by G. Frebold, J. C. Zimmermann, O. Luedecke, J. C. L. Zincken, W. Geilmann and H. Rose, and H. Rose; in Saxony, by A. Frenzel, and C. M. Kersten; in the Argentine, by I. Domeyko, and A. Stelzner; and in Spain, by A. Breithaupt. Analyses reported by F. Stromeyer and J. F. L. Hausmann, H. Rose, C. F. Rammelsberg, and I. Domekyo are close to requirements for lead monoselenide, PbSe, with up to 3·14 per cent. of cobalt. The mineral is lead-grey, and occurs in fine granular masses, sometimes foliated, and rarely in cubical crystals, with cubic cleavage. The artificial selenide may appear as a black powder, in needles, rectangular plates, or cubical crystals or prisms, lead-grey or bluish-black in colour. S. von Olshausen found that the X-radiogram agrees with the face-centred cubic lattice of the cæsium chloride type with side a=6·162 A., and sp. gr. 8·139. L. Pauling, and L. S. Ramsdell studied this subject. F. Stromeyer and J. F. L. Hausmann gave 7·697 for the sp. gr. of the mineral. C. M. Kersten gave 7·70 to 7·71, and A. Stelzner, 7·6. For the artificial fused selenide G. Little gave 8·154, H. Fonzes-Diacon, 8·10 for the crystals at 15°, and F. A. Henglein and R. Roth, 8·07; and F. A. Henglein gave 35·3 for the mol. vol. The hardness of the mineral is about 2·5. K. Friedrich and A. Leroux, and H. Pélabon, gave 1065° for the m.p. C. Fabre gave 15·76 Cals. for the heat of formation of crystalline lead selenide, and 12·96 Cals. for the precipitated selenide. A. de Gramont examined the spark spectrum. W. Herz gave $3·29 \times 10^{12}$ for the vibration frequency of PbSe. F. Beijerinck, and R. G. Harvey found that it is an electrical conductor. E. T. Wherry found clausthalite to be a fair radio-detector. T. W. Case found that its resistance is less than a megohm, and is not affected by light. H. Fonzes-Diacon said that lead selenide can be sublimed in hydrogen without reduction. Clausthalite decrepitates when heated; and, according to J. J. Berzelius, when both the natural and the artificial selenide are heated in a closed tube, selenium and lead selenide sublime. H. Fonzes-Diacon found that when the selenide is heated in air, selenium dioxide, and lead oxide are formed, while water vapour, at a red-heat, reacts with part of the selenide to form hydrogen selenide and lead oxide; part is reduced to lead, and part sublimes as lead selenide. J. Joly observed a red sublimate at 340° in air, and a white one at 600°. The selenide is decomposed by chlorine, forming lead chloride and selenium chloride; at a red-heat, hydrogen chloride forms hydrogen selenide and lead chloride; while conc. hydrochloric acid attacks the mineral only when the acid is boiling. J. C. L. Zincken, and H. Fonzes-Diacon observed that conc. sulphuric acid forms a brown, green, or reddish-brown soln.—coloured by selenium—and lead sulphate. J. J. Berzelius, and H. Fonzes-Diacon found that cold nitric acid dissolves the selenide with the separation of selenium, which dissolves if the acid is warm; fuming nitric acid dissolves the selenide as lead selenate. H. Fonzes-Diacon found that phosphorus trichloride at a dull red-heat produces selenium dichloride. H. C. Bolton said that a sat. soln. of citric acid dissolves clausthalite in the cold. W. Geilmann and H. Rose observed that when clausthalite is treated with mercuric chloride at 300°, a solid crust of mercuric selenide grows on the surface: $PbSe+HgCl_2=HgSe+PbCl_2$.

The mineral **zorgite** occurs in granular masses resembling clausthalite at Zorge and Tilkerode in the Harz. H. Rose called it *Selenblei mit Selenkupfer*; J. C. L. Zincken, *Selenkupferblei*, and *Selenbleikupfer*; E. F. Glocker, *Selenkupferbleiglanz*; W. H. Miller, *zorgite*; F. von Kobell, *rhaphanosmite*—from ῥαφανίς, radish, and ὀσμή, smell. Analyses were reported by H. Rose, C. F. Rammelsberg, C. M. Kersten, F. Pisani, and F. Heusler and H. C. Klinger. F. Pisani represented some samples by (Pb,Cu)Se, and others by $(Cu,Pb)_3Se_2$; C. Klein, and A. Arzruni found a sample agreeing neither with (Pb,Cu)Se nor with $(Pb,Cu_2)Se$, but rather with a mixture of PbSe, 4CuSe, and 3Cu,Se. It is therefore probable that zorgite is a mixture of lead and copper selenide. K. B. Roger found that zorgite is decomposed by heating it at 200° to 450° in the vapour of carbon tetrachloride and air. M. Adam's *cacheutaite* from Cacheuta, Argentine, is a variety of this mineral. The dark or light grey granular masses of zorgite have a sp. gr. 7·00–7·55, and a hardness of 2·5.

Another mineral from Tilkerode and Lerbach, Harz, was described by H. Rose, *Selenblei mit Selenquecksilber*, and J. C. L. Zincken called it *Selenquecksilberblei*; E. F. Glocker, *Selenquecksilberbleiglanz*; and W. H. Miller, **lerbachite**. Analyses were reported by H. Rose, and C. F. Rammelsberg, and are usually represented by (Hg,Pb)Se. It is probably a mixture of lead selenide with mercury selenide and more or less copper selenide. A. Streng found thallium in a sample from Lehrbach. The lead-grey, steel-grey, or iron-black mineral occurs in granular masses of sp. gr. 7·08–8·11, and hardness 2·5. C. F. Rammelsberg described a copper-mercury-lead selenide from Zorge, Harz, which has a composition ranging from $2PbSe.4CuSe.Cu_2Se.HgSe$ to $8PbSe.37Cu_2Se.HgSe$. It appears to be a mixture which has been called *seebachite*. R. G. Harvey measured the electrical resistance.

F. Wöhler[15] prepared **nitrogen selenide,** or **selenium nitride**, which, according to a subsequent analysis of A. Verneuil, has the composition NSe; and, by analogy with nitrogen sulphide, has the mol. formula, N_4Se_4 (*q.v.*). W. Strecker and L. Claus decided that it is not a derivative of azoimide, and favoured the cyclic formula Se_4N_4. This agrees with the mol. wt. determined by H. B. van Valkenburgh and J. C. Bailar from its effect on the f.p. of a soln. in glacial acetic acid. W. Strecker and L. Claus did not obtain satisfactory results with diphenyl, naphthol, and liquid sulphur dioxide. F. Wöhler made it by passing dry ammonia, dil. with air or hydrogen, over selenium tetrachloride cooled by a mixture of ice and salt. The tetrachloride forms a green and then a brown spongy mass consisting of undecomposed tetrachloride, selenium, ammonium chloride, and nitrogen selenide. There is a danger of an explosion during the operation. The product is agitated with a large proportion of water, and the brick-red powder is separated, dried, and washed with carbon disulphide, or a dil. soln. of potassium cyanide to remove the selenium. R. Espenschied also employed this mode of preparation; while A. Verneuil said that the product is not constant in composition, and he preferred the following procedure:

Ten grams of selenium tetrachloride are triturated with a few drops of carbon disulphide, and then suspended in about a litre of that liquid. Only a little tetrachloride dissolves. A current of dry ammonia is then passed through the liquid with frequent stirring. The liquid is coloured rose-red, and then cochineal-red; as the current of gas continues, brown flecks appear, and by continuing the passage of the gas, these flecks assume a pale orange-yellow colour. The liquid then smells strongly of ammonia, some nitrogen is given off about the middle of the operation: $6SeCl_4+32NH_3=6NSe+24NH_4Cl+N_2$. The mixture is filtered, and the solid is washed with carbon disulphide, squeezed, and dried in a current of air. The ammonium chloride is removed from the orange-yellow powder by washing with water, drying in air, and finally washing with hot carbon disulphide. The yield is 80 per cent.

H. B. van Valkenburgh and J. C. Bailar obtained nitrogen selenide by the action of dry ammonia on a dil. soln. of selenium monochloride in carbon disulphide. F. W. Bergstrom found that selenium has an extremely slight solubility in liquid ammonia, and the character of the soln. resembles that of sulphur in the same solvent—*i.e.* selenium tends to react with ammonia, producing nitrogen selenide and ammonium selenide. W. Strecker and L. Claus did not obtain good yields of nitrogen selenide with liquid ammonia and selenium monochloride, or the tetrachloride. In the presence of carbon disulphide as a solvent, selenium tetrahalides give better yields of nitride than do the lower halides or the oxyhalides. The results with selenium tetrabromide were better than with the tetrachloride. The equation given by A. Verneuil gives far too small a proportion of nitrogen for that actually evolved in the case of selenium tetrabromide. When benzene is used as a solvent, the reaction appears to be $3SeBr_4+16NH_3=2SeN+Se+N_2+12NH_4Br$. A. Michaelis showed that selenyl chloride reacts with dry ammonia: $6SeOCl_2+16NH_3=3SeO_2+3Se+2N_2+12NH_4Cl$; and V. Lenher and E. Wolesensky found that if a conc. soln. of selenyl chloride in benzene or toluene be treated with dry ammonia, a large proportion of the selenium is precipitated; but with a dil. soln. (2–4 per cent.) in benzene, a buff-coloured precipitate is formed; this becomes orange-red when dry. When washed with water, and with a soln. of potassium cyanide to remove selenium, brick-red nitrogen selenide is formed. The amorphous, orange-yellow powder is very hygroscopic, and, according to A. Verneuil, when dried in air, retains only 0·15 per cent. of ammonia. When dry, a very slight press. suffices to produce an explosion. According to R. Espenschied, the explosive decomposition of nitrogen selenide into its elements is accompanied by red fumes of selenium, and there is a smell of hydrogen sulphide; the colour of the powder does not change at 150°, but it explodes at 200°. W. Strecker and L. Claus gave 160° as the explosion temp.; V. Lenher and E. Wolesensky, 130°; and A. Verneuil added that at 230° it explodes as easily as fulminating silver, and less easily than nitrogen iodide. M. Berthelot and P. Vieille gave for the heat of formation (N,Se)=42·3 Cals. at constant press., and 42·6 Cals. at constant vol. According to A. Verneuil, and R. Espenschied, nitrogen selenide is insoluble in water, ether, and absolute alcohol; and very sparingly soluble in carbon disulphide, benzene, and acetic acid. It is not changed by cold water; but when heated with water to 150°–160°, it is hydrolyzed to selenious acid, selenium, and ammonia. Warm, conc. potash-lye decomposes the selenide into selenium, potassium selenite and selenide, and the whole of the nitrogen is set free as ammonia; with hydrochloric acid, ammonium selenite and selenide are formed. According to W. Strecker and L. Claus, chlorine and bromine react explosively with selenium nitride. In the presence of carbon disulphide, the action of bromine leads to the formation of a brownish-green, hygroscopic substance, SeN_2Br. Bromine vapour dil. with carbon dioxide transforms solid selenium nitride into ammonium selenohexabromide, $(NH_3)_2SeBr_3$, the formation of which appears to be due to the action of atm. moisture on a primary additive product of bromine and the nitride. Chlorine, in similar circumstances, gives the product $SeNCl_3$. Bromination of the compound Se_2N_2Br yields the substance SeN_3Br_4, whereas exhaustive chlorination of the product Se_2NCl yields Se_2NCl_2, which possibly is not quite homogeneous. Selenium nitride is not affected by solid iodine or by a soln. of the halogen in ether or chloroform. If partly wetted with fuming hydrochloric acid, or if treated with hydrogen chloride, or with chlorine, an explosion occurs. With sodium hypochlorite, nitrogen is given off and sodium selenate is formed. A dil. soln. of selenic acid is reduced by nitrogen selenide, forming selenious acid, selenium, and ammonia; likewise also with cold or hot nitric acid, in which case the selenium dissolves. H. B. van Valkenburgh and J. C. Bailar found that when ammonia is passed through a soln. of nitrogen tetraselenide in carbon disulphide for half an hour, a red soln. is formed. On evaporation, this yields a dark red, heavy liquid, very similar to the compound formed by ammonia and nitrogen tetrasulphide in the same manner.

According to J. J. Berzelius,[16] selenium and phosphorus are miscible in all proportions when heated to temp. near the m.p. of phosphorus. When a large proportion of selenium is present, the dark brown, fusible mass has a conchoidal fracture; and when the product containing an excess of phosphorus was heated, phosphorus and a small proportion of selenium distilled off. The phosphorus selenide forms a little hydrogen selenide with water; and it dissolves in potash-lye, forming potassium selenide and phosphate. J. Meyer found that mixtures of 4·4 parts of phosphorus with 0·5, 1·0, 2·0, and 3·0 parts of selenium melt respectively at 35°, 27°, 9°, and at −7°. O. Hahn reported the four phosphorus selenides, with the at. proportions P : Se=4 : 1, 2 : 1, 2 : 3, and 2 : 5 respectively.

Of these, J. Meyer said that the first two are mixtures and not chemical individuals, and that the third may or may not be a compound. He prepared the selenides P_4Se_3 and P_2Se_3. The equilibrium diagram has not been explored, so that the question is still an open one.

O. Hahn melted a mixture of one gram-atom of selenium with 4 gram-atoms of phosphorus in an atm. free from oxygen, and pressed the product through a fine linen cloth, under water, to remove red phosphorus. He considered it to be **phosphorus tetritaselenide,** P_4Se. J. Meyer was unable to obtain a product not contaminated with free selenium and red phosphorus. O. Hahn described it as a thick, oily, dark yellow mass with a nasty smell resembling that of phosphorus trioxide and hydrogen selenide. It freezes below −17° to a crystalline mass, and melts at −7°. When heated, J. Meyer observed that phosphorus alone distils over, leaving a residue richer in selenium. O. Hahn found that the product ignites in air, burning with a luminous flame, which emits a white smoke. It can be kept for some time under air-free water, but if air be present, it acquires an opaque crust which forms phosphoric acid and presumably selenious acid with the water. Red fuming nitric acid inflames the product. It is freely soluble in carbon disulphide, and it acts on alcohol, and ether. Cold alkali-lye has no action, but when boiling, phosphine, alkali phosphite, selenite, and selenide are formed. With cold soln. of metal salts the tetritaselenide slowly acquires a film of the metal phosphide and selenide, and this occurs rapidly when the mixture is heated.

O. Hahn also obtained **phosphorus hemiselenide,** P_2Se, in an analogous manner, using the correct proportions of the two elements. Much heat is developed, and some of the product sublimes, while most of it immediately solidifies. At ordinary temp., the hemiselenide is a pale red solid, which, in thin layers, appears reddish-yellow, and when powdered, its colour resembles that of precipitated antimony sulphide. The solid has a conchoidal fracture, and its smell recalls that of hydrogen selenide. It reddens moist litmus paper. It is stable in dry air, but in moist air, the phosphorus oxidizes, and hydrogen selenide is given off. The heat of the reaction may suffice to inflame the product. When heated, sublimation occurs. J. Meyer found that when the hemiselenide is heated in an atm. of carbon dioxide at ordinary press., phosphorus contaminated with selenium first distils over, and finally dark red vapours of the tritetritaselenide. O. Hahn said that carbon disulphide removes variable amounts of phosphorus, while alcohol and ether have no solvent action. Boiling alkali-lye forms phosphine, leaving a red residue containing phosphorus and selenium. The behaviour with soln. of the metal salts resembles that with the tetritaselenide.

J. Meyer obtained **phosphorus tetritatriselenide,** P_4Se_3, as indicated above, during the distillation of the alleged hemiselenide ; by distilling the hemitriselenide ; and also by melting a mixture of the component elements in the right proportions, at 215° to 220°, and purifying the product by distillation. The compound separates from its soln. in carbon disulphide in orange-red crystals. They have a smell recalling phosphine and also hydrogen selenide. According to J. Mai, this compound is readily obtained by the action of yellow phosphorus on powdered selenium in boiling tetrahydronaphthalene ; and purifying the crude crystals by extraction with a mixture of carbon disulphide and light petroleum. The selenide appears to exist in two modifications, but the tetrahydronaphthalene reduces the temp. of reaction to such an extent that only the form stable at the lower temp. is obtained. The sp. gr. is 1·31 ; the m.p. is 242°. J. Meyer found that the b.p. is 360° to 400°. It phosphoresces at 160°, and more strongly at a higher temp. In air, and possibly also under the influence of light, the tetritatriselenide acquires a yellow film of what is probably finely-divided selenium. The compound inflames when heated in air, forming phosphorus pentoxide, and selenium dioxide. It is very sensitive towards moisture. Moist air forms hydrogen selenide. Water has but little action. Sulphuric acid forms a green soln. ; and nitric acid oxidizes it readily. It is soluble in carbon tetrachloride and disulphide, chloroform, benzene, toluene, acetone, and acetylene di- and tri-chlorides ; and it can be crystallized from these solvents under press. ; in air, the yellow soln. deposits selenium. With conc. potash-lye, it forms phosphine, and a dark red liquid containing potassium polyselenide, and hypophosphite which, in air, deposits red selenium.

O. Hahn, W. Muthmann and A. Clever, and J. Meyer obtained *phosphorus sesquiselenide*, or **phosphorus hemitriselenide,** P_2Se_3, by warming a mixture of the constituent elements in the right proportions. According to O. Hahn, the dark, ruby-red mass appears pale red in thin layers, and looks like red phosphorus when powdered. It does not change in dry air, but slowly oxidizes in moist air; W. Muthmann and A. Clever added that it is not quite stable in dry air; and in moist air, it forms hydrogen selenide and phosphorous acid. J. Meyer found that when heated it decomposes into the tetritatriselenide and the pentaselenide. O. Hahn observed that the tetritatriselenide burns in air with a pale flame, forming red fumes; and it forms a little hydrogen selenide when treated with boiling water. A little hydrogen selenide is formed when the tetritatriselenide is treated with acids; the compound dissolves freely in cold alkali-lye; and less readily in soln. of alkali carbonates; W. Muthmann and A. Clever said that selenophosphates are produced by the action of alkali-lye.

W. Bogen prepared **phosphorus pentaselenide,** P_2Se_5, by melting a mixture of the two elements in an atm. of carbon dioxide; O. Hahn, and W. Muthmann and A. Clever used a similar process. J. Meyer obtained it as a residue in the distillation of the tetritatriselenide. A. Besson found that hydrogen selenide reacts slowly with phosphoryl chloride forming, in the course of 8 days, this sulphide: $4POCl_3+5H_2Se=10HCl+2PO_2Cl+P_2Se_5$. The dark red or black mass was found by B. Rathke to crystallize from carbon tetrachloride in black needles. O. Hahn found that the pentasulphide burns in air, forming a dense, red smoke; and when distilled, vapours rich in phosphorus are first evolved, and afterwards selenium. O. Hahn said that the pentasulphide is stable in air, but W Muthmann and A. Clever added that it is not quite stable in air because the powder always smells of hydrogen selenide, and it rapidly attracts moisture, forming hydrogen selenide and phosphoric acid. B. Rathke found that steam or boiling water slowly forms hydrogen selenide and phosphoric acid. O. Hahn stated that the pentasulphide is insoluble in carbon disulphide; B. Rathke found that dry carbon tetrachloride does not decompose it at 200°, but with the moist tetrachloride, carbon diselenide is formed. W. Bogen represented the reaction which occurs when the pentasulphide is warmed with alcohol, by $P_2Se_5+5C_2H_5OH=H_2Se+H_2O+(C_2H_5)_3O_2Se.PSe+(C_2H_5)_2H.O_2Se.PSe$. C. Paal studied the reaction with acetonylacetone. B. Rathke said that with conc. potash-lye the reaction can be represented: $P_2Se_5+16KOH=2K_3PO_4+5K_2Se+8H_2O$; and W. Muthmann and A. Clever observed that selenophosphates are formed. O. Hahn observed that when mixtures of phosphorus pentaselenide and the metal selenides are fused, phosphoselenides are formed. According to J. Mai, when iodine is added to a soln. of phosphorus selenide in carbon disulphide, **phosphorus diiodotriselenide,** $P_4I_2Se_3$, is formed. It melts at 154°–155° when rapidly heated. **Phosphorus sulphoselenide** was also prepared.

J. J. Berzelius[17] observed that molten selenium gradually dissolves arsenic, forming when cold a black, fusible mass which bubbles and boils at a red-heat, giving off the vapour of what appears to be a perselenide of arsenic; the bubbling then ceases and no further change occurs until a white-heat is attained, when the product distils over in drops which solidify to a dark brown, shiny mass with a conchoidal fracture. G. Little, and H. Pélabon obtained brittle, vitreous masses by fusing together different proportions of the two elements. E. Szarvasy prepared what appeared to be the most stable compound of arsenic, namely **arsenic hemiselenide,** As_2Se, by melting the two constituents in the requisite proportions, or with a very slight excess of arsenic, the operation being carried out in a sealed tube filled with nitrogen. The combination took place at about 600°, and the product, which consisted mainly of the monoselenide, was sublimed under press. in an atm. of nitrogen. The vapour density at 617° corresponds with the formula As_4Se_2, but at 1002° it corresponds with the formula As_2Se, and above this temp., dissociation of the compound into its own elements occurs. E. Szarvasy and C. Messinger gave 15·48 at 617° when the normal value for As_4Se_2 is 15·84; this falls to 7·55 at 1159°—theory for As_2Se, 7·92. According to E. Szarvasy, the hemiselenide forms black, metallic-looking crystals, giving a black streak. It is insoluble in the usual organic and inorganic solvents; conc. hydrochloric and sulphuric acids act on it slowly, boiling alkali hydroxides, however, decompose it, in much the same manner as they do the lower sulphides of arsenic.

H. Uelsmann melted arsenic and selenium in the proportions required for **arsenic triselenide,** As_2Se_3, and obtained a black, amorphous mass which dissolves in soda-lye, leaving bronze-coloured plates behind; he obtained a dark brown precipitate by passing hydrogen selenide into a soln. of arsenic trioxide feebly acidified. The trisulphide forms a reddish-brown powder which melts at 260° to a black liquid which freezes to an amorphous solid. H. Pélabon said that hydrogen has an appreciable action on arsenious selenide, As_2Se_3, even at 440°, and when excess of the selenide is employed the limiting value of the characteristic ratio is 7·9; at 610°, this value increases to 13·5. The interaction of hydrogen with a mixture of selenium and arsenic at 610° decreases rapidly as the proportion of the latter metalloid increases. L. Moser and K. Atynsky obtained it by the action of an arsenic salt on a soln. of hydrogen selenide protected from air. According to H. Uelsmann, the trisulphide is soluble in nitric acid with the separation, at first, of red selenium; alkali-lye dissolves it, forming a reddish-brown liquid; and alkali sulphide solns. dissolve the triselenide without forming selenoarsenites, but W. Muthmann and A. Clever did obtain Na_3AsSe_3—*vide infra*, selenoarsenites. C. Lausen described **jeromite** as a mineral occurring in black fused globules on rock crevices from which hot gases issue in the United Verde Mine at Jerome, Arizona. Thin splinters are cherry-red, and optically isotropic. The composition approximates **arsenic diselenide,** $As(Se,S)_2$. It is insoluble in nitric acid.

W. Muthmann and A. Clever prepared what they regarded as **arsenic pentaselenide,** As_2Se_5, by heating the requisite proportions of the constituent elements. E. Szarvasy melted the mixture at about 400° in a sealed tube containing nitrogen, and purified the black, lustrous, brittle mass by distillation under reduced press. The treatment of the product with carbon disulphide does not purify it so well. W. Muthmann and A. Clever obtained the pentasulphide, as a reddish-brown powder, by treating potassium trioxypentaselenodiarsenate with acids. L. Moser and K. Atynsky obtained it by a process analogous to that used for the triselenide. E. Szarvasy and C. Messinger found that the vapour density at 800° is 9·59 when the normal value is 18·84; and it is 7·41 at about 900°. This corresponds with the dissociation into two mols., and at higher temp., *viz.* 1050°–1100°, it appears to dissociate into three mols.: $As_2Se_5 = As_2Se + 2Se_2$. W. Muthmann and A. Clever, and E. Szarvasy found that the pentaselenide decomposes when heated in air, forming red selenium and a greyish-black sublimate. It is not acted upon by ordinary solvents. It is insoluble in water; it forms a greenish-red soln. with aq. ammonia; it dissolves in soln. of alkali hydroxides and sulphides, but the yellow liquids decompose when exposed to air, and when acidified with mineral acids give a reddish-brown flocculent precipitate of the pentasulphide. The pentasulphide is insoluble in dil. acids and conc. hydrochloric acid, and is slowly decomposed by warm, dil. nitric acid, very rapidly by cold, fuming nitric acid, whereby arsenic and selenious acid are formed. It is insoluble in warm alcohol, ether, and carbon bisulphide, and has neither taste nor odour. The pentaselenide forms selenoarsenates—*vide infra*—when treated with alkali selenide, and sulphoselenoarsenates—*vide infra*—when treated with alkali sulphides.

J. J. Berzelius[18] observed that antimony and selenium readily unite on the application of heat; the mass frequently becomes red-hot during the combination. The product is a lead-grey mass with a crystalline fracture, and fusing at a red-heat. When heated in air, it gives off a little selenium and forms a vitreous slag. According to H. Pélabon, the cooling curve of mixtures with 11–39 per cent. of selenium have two f.p., 566° and 518° respectively. There is a maximum in the f.p. curve at 605°, corresponding with the triselenide; and a point of inflexion on the cooling curve corresponds with antimony heptaselenide, Sb_2Se_7. P. Chrétien added that the two f.p. observed by H. Pélabon are due to ineffectual stirring; the two temp. represent the m.p. of two mixtures, the liquid not being homogeneous, but consisting of two phases, for on analyzing a mixture which had the two m.p. 523° and 560°, the lower part contained 12·69 and the middle part 32·12 per cent. of selenium. N. Parravano's observations are summarized in Fig. 43. He also obtained only one compound, antimony triselenide, which does not mix in all proportions with antimony. The two liquid layers in equilibrium contain respectively 11 and 35 per cent. of selenium. The two non-miscible liquids have so small a difference in density that they do not separate completely during cooling. The discontinuity, observed by H. Pélabon, is explained not by the formation of an heptaselenide, but is due to the partial miscibility of the triselenide with selenium. M. Chikashige and M. Fujita found a maximum in the f.p. curve at 572° corresponding with the formation of antimony selenide. This compound forms a eutectic at 497° with 46·5 per cent. of antimony, and the eutectic at 211° is very near the value for selenium itself.

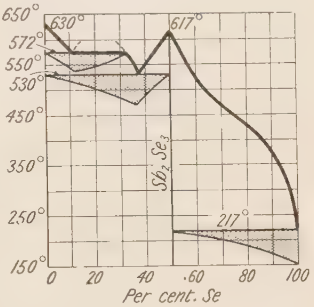


FIG. 43.—Freezing-point Curve of the Binary System: Antimony–Selenium.

J. J. Berzelius, G. Hofacker, H. Uelsmann, H. Pélabon, P. Chrétien, N. Parravano, etc., prepared **antimony triselenide,** Sb_2Se_3, by the direct union of the elements; and the conditions of formation are illustrated in Fig. 43. J. J. Berzelius also made it by the action of hydrogen selenide on a soln. of potassium antimonyl tartrate. L. Moser and K. Atynsky used an analogous process. H. Uelsmann said that the black powder suddenly sinters at about 140°, and melts at a red-heat, and freezes to a grey, crystalline mass. H. Pélabon gave 605° for the m.p.; P. Chrétien, 611°; N. Parravano, 617°; and M. Chikashige and M. Fujita, 572°. P. Chrétien studied its reduction by hydrogen. H. Uelsmann said that it forms a brown soln. with hot potash-lye. H. Pélabon measured the electrical resistance of the alloys, and found that the sp. resistance varies with the composition, temp., and the previous history of the alloys. Thus, with the Sb : Se-alloy:

	35°	161°	276°	388°	495°	524°
R .	0·0939	0·1059	0·1350	0·1559	0·1768	0·1991 ohms.

The resistance of alloys with more antimony increases less rapidly, but nearly proportionally with the temp.; while the resistance of alloys containing more selenium increases regularly with the temp. up to a maximum, and then decreases to a minimum. The results are different according as the temp. is rising or falling. Thus:

	Heating.					Cooling.			
	15°	124°	313°	360°	440°	339°	217°	157°	15°
R .	0·198	0·225	0·292	0·301	0·265	0·346	0·351	0·297	0·221

M. Padoa also studied the electrical conductivity, and found a maximum corresponding with Sb_2Se_3. The e.m.f. of a cell with electrodes of antimony and antimony in a soln. of antimony trichloride acidulated with hydrochloric acid, varies with time, for at the start it was 0·0606 volt; after being kept one day, 0·08306 volt; 2 days, 0·0875 volt; 15 days, 0·1139 volt; and after 30, 56, and 65 days, respectively 0·1192, 0·1199, and 0·1197 volt. With alloys containing Sb : Se in the molar ratio:

Sb : Se .	999 : 1	99 : 1	9 : 1	3 : 1	2 : 1	1 : 1	3 : 4	2 : 3
Volts .	0·052	0·055	0·083	0·079	0·103	0·104	0·121	0·332

and alloys richer in selenium have the constant e.m.f. of 0·33 volt. R. Kremann and P. Wittek's results with the cell are plotted in Fig. 44. The singular points indicate the existence of the mono- and tri-selenides. H. Pélabon found that the cells are sensitive to light. The e.m.f. rises sharply on illumination and then drops slowly, the drop becoming sharp when the source of light is removed. The red rays are the most active in promoting this effect. With the cell in open circuit the e.m.f. diminishes gradually with rise in temp., but in closed circuit the e.m.f. increases rapidly as the temp. rises. The thermoelectric force of the Sb : Se-alloys against platinum with the cold junction at 11°, and the hot junction at a temp. $\theta°$, shows a maximum corresponding with the presence of the triselenide, and in the case of the compound itself, the thermoelectric force is ten times as great at all temp. as those of mixtures differing even only slightly in selenium content from the compound. Further, antimony triselenide, like other metallic selenides, has a very high thermoelectric force in the solid state. With antimony itself, or with the mixtures, there is no sudden change in the thermoelectric force when one element of the couple melts. For example, the thermoelectric forces of couples with platinum and antimony alone, and with antimony triselenide, are:

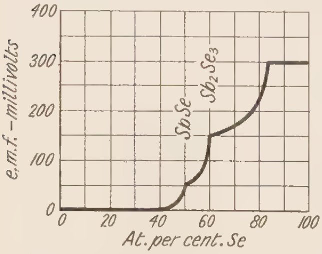


FIG. 44.—Electromotive Force of the Sb | $SbCl_3$ | $SbSe_n$-cell.

θ . .	162°	270°	376°	518°	645°	711°	844°
Sb . .	0·0071	0·0128	0·0189	0·0256	0·0302	0·0315	0·0315
Sb_2Se_3 .	0·123	0·197	0·272	0·364	0·402	0·403	0·392

G. Hofacker obtained what he regarded as **antimony pentaselenide,** Sb_2Se_5, by the action of hydrochloric acid on a soln. of sodium orthoselenoantimonate; if air has access, some selenium is formed. If the brown powder is heated, some selenium is given off. It is reduced with difficulty by hydrogen; it is soluble in potash-lye; and forms seleno-salts with the metal selenides—*vide* selenoantimonites and selenoantimonates. L. Moser and K. Atynsky could not prepare the pentaselenide by the action of antimonic salt on a soln. of hydrogen.

According to P. Chrétien, the cooling curve of alloys of antimony and selenium shows four maxima: one corresponds with the triselenide, Sb_2Se_3; another with *antimony monoselenide*, SbSe, melting at 542°; a third with *antimony tetritapentaselenide*, Sb_4Se_5, melting at about 590°; and the fourth with *antimony tritatetraselenide*, Sb_3Se_4, melting at about 605°. He also said that the complete reduction of antimony triselenide by hydrogen proceeds step by step: $Sb_2Se_3 \rightarrow Sb_3Se_4 \rightarrow Sb_4Se_5 \rightarrow SbSe$. He said that the relative velocities of the reduction of Sb_2Se_3, Sb_4Se_5, and SbSe are represented respectively by 28, 4·3, and 1. The existence of none of the alleged selenides—Sb_3Se_4, Sb_4Se_5, and SbSe—could be detected by N. Parravano, or by M. Chikashige and M. Fujita; and M. Parravano said that they merely represent mixtures of antimony trisulphide with selenium. R. Kremann and R. Wittek said that the e.m.f.-composition curve, and the microscopic structure indicate the existence of the mono- and the tri-selenides.

J. J. Berzelius[19] observed that when bismuth and selenium are heated together, they unite with the faint evolution of light, and heat, to form a silver-white alloy with a crystalline fracture, and fusing at a red-heat. H. Pélabon inferred that **bismuth monoselenide,** BiSe, shows itself as a singular point at 625° on the f.p. curve of mixtures of selenium and bismuth; and this compound can mix in the liquid state with an excess of bismuth, and when heated with selenium in a sealed tube it forms bismuth triselenide. H. Pélabon prepared the monoselenide by fusing together its constituents in eq. proportions. It is slightly decomposed by hydrogen at 610°, but the change is limited by the inverse action; the characteristic ratio of the proportion of hydrogen selenide to the total hydrogen present for equilibrium is 3·34, but this value rapidly diminishes to zero as the amount of bismuth is increased. N. Parravano's observations on the f.p. curve of bismuth and selenium show that there is a discontinuity at about 73 per cent. of bismuth and 600°–610°, and a maximum at about 63 per cent. of bismuth and 706°, which corresponds with the compound Bi_2Se_3. As the proportion of selenium is further increased, the curve falls, then remains horizontal, and finally descends to the m.p. of selenium. The thermal effect which mixtures containing 63–73 per cent. of bismuth show at 600°–610° is attributed to the existence of bismuth monoselenide. N. Tomoshige's observations are summarized in Fig. 45. C. Hutchins studied this subject. The triselenide is represented by a maximum on the liquidus curve at 688°. The triselenide mixes with an excess of bismuth in the liquid state, and on cooling crystallizes out until the temp. reaches 602°, at which point a reaction takes place between the compound and bismuth with the formation of the β-form of the monoselenide, BiSe, the reaction taking place with development of heat. On further cooling, the monoselenide continues to crystallize out down to 422°, the transition point, at which it changes into the α-form. The final eutectic temp. on the bismuth side is practically the m.p. of bismuth, 267°. On the selenium side of the diagram the triselenide forms a homogeneous liquid with 14 per cent. of selenium, and at 604° it deposits the monoselenide. With more than 51 per cent. of selenium two layers are formed, the above homogeneous liquid being in equilibrium with a soln. of selenium containing 9 per cent. of bismuth. On cooling, the trisulphide is deposited until one liquid layer disappears; the other then deposits the compound, and finally crystallizes as a eutectic at 161°. There is no sign on the fusion curve of the existence of F. Rössler's *bismuth hemiselenide*, Bi_2Se, said to be formed, in octahedral crystals, by melting selenium with an excess of bismuth (1 : 20) and separating the excess of bismuth with cold, dil. nitric acid.

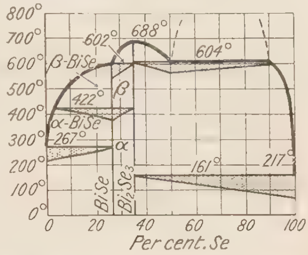


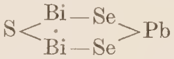
FIG. 45.—Freezing-point Curves of the Binary System: Bi–Se.

In 1873, A. del Castillo described *una nueva especie mineral de bismuto* from Guanajuato, Mexico; and, shortly afterwards, V. Fernandez the occurrence of a bismuth selenide containing some zinc, which he called **guanajuatite.** A. Frenzel called it *Selenwismuthglanz*; J. D. Dana, *frenzelite*—after A. Frenzel; and I. Domeyko, *castillite*—A. del Castillo. H. Rose and co-worker described a deposit at Andreasberg. Analyses reported by H. Rose, V. Fernandez, C. F. Rammelsberg, J. W. Mallet, A. Frenzel, and F. A. Genth agree with the formula for **bismuth triselenide,** Bi_2Se_3, contaminated with more or less bismuth trisulphide –a little zinc and iron compounds may be present, and A. de Gramont detected spectroscopically thallium and copper. The bluish-grey mineral *silaonite* stated by V. Fernandez and S. Navia to occur near guanajuatite was represented as having the composition Bi_3Se; the analyses of H. D. Bruns indicated a composition nearer Bi_8Se_3; and both J. D. Dana, and V. Fernandez later agreed that it is not a homogeneous individual, but rather a mixture of metallic bismuth and bismuth trisulphide. The sp. gr. is 6·43–6·45, and the hardness 3.

Bismuth triselenide was prepared, as a steel-grey, crystalline mass, by J. J. Berzelius, G. Little, R. Schneider, H. Pélabon, and N. Parravano by the direct union of the elements; and the conditions under which it is formed are indicated in M. Tomoshige's diagram, Fig. 45. A. Hilger and P. A. van Scherpenberg obtained it by adding bismuth trioxide to a soln. of selenium in molten potassium hydroxide. The mass becomes red, and, when exposed to air, black. The black powder is washed with water containing a little alkali. H. Uelsmann prepared the triselenide by passing hydrogen selenide into a soln. of bismuth nitrate containing as little free nitric acid as possible. L. Moser and K. Atynsky used an analogous process. Guanajuatite is bluish-grey and it occurs in compact, granular, foliated, or fibrous masses, as well as in rhombic, bipyramidal crystals which, according to A. Frenzel, are isomorphous with stibnite and bismuthinite. The acicular, prismatic crystals may be striated longitudinally, and form semi-compact masses; the (010)-cleavage is distinct. A. del Castillo gave 5·15 for the sp. gr. of the mineral; A. Frenzel, 6·25; V. Fernandez, 6·62; E. Wittich, 6·25–6·97; C. F. Rammelsberg, 6·845; and F. A. Genth, 6·977. R. Schneider gave 6·82 for the sp. gr. of the artificial trisulphide. A. del Castillo gave 2 for the hardness; A. Frenzel, 2·5–3·0; and

V. Fernandez, 3·5. J. J. Berzelius, and H. Uelsmann said that the artificial triselenide melts at a red-heat, and, according to R. Schneider, this occurs with the loss of selenium; L. H. Borgström gave 690° for the m.p. H. Pélabon gave about 717° for the m.p.; N. Parravano, 706°; and M. Tomoshige, 688°. A. de Gramont studied the spark spectrum of the mineral. F. Beijerinck, and R. G. Harvey, said that the mineral is a conductor of electricity. E. Becquerel made observations on the thermoelectric properties of the alloy. E. T. Wherry found guanajuatite to be a fair radio-detector. R. Schneider, and G. Little observed that the triselenide gives off selenium and forms a black oxide when heated in air; it is scarcely attacked by hydrochloric acid—cold or boiling; it is attacked only a little by dil. nitric acid, but the conc. acid, and aqua regia, decompose it easily and completely; it is converted by molten potassium nitrate into bismuth oxide and potassium selenate; and, according to H. Uelsmann, it dissolves in molten ammonium bismuth chloride to form bismuth selenochloride. A. Hilger and P. A. van Scherpenberg observed that with fused potassium carbonate a metaselenobismuthite is formed; and F. Rössler, that with silver selenide it forms a silver selenobismuthite.

M. Weibull described a mineral from the Fahlun mines, Sweden, and analyses were also reported by F. A. Genth, and T. L. Walker. G. Flink called it **weibullite.** M. Weibull represented the composition by $PbS.Bi_2S_3.PbS.Bi_2Se_3$; F. A. Genth, by $Pb(Se,S).Bi_2(Se,S)_5$; P. Groth and K. Mieleitner by $PbBi_2(S,Se)_4$; and G. Flink, by $2PbS.Bi_4Se_3S_3$. It occurs in lead-grey plates. F. A. Genth gave 7·245 for the sp. gr.; G. Flink, 6·97, and 2–3 for the hardness. G. Flink described crystals of graphite-black mineral from Faben, and he called it **platynite**—from πλατιγεῖν. Its composition is $PbS.Bi_2Se_2$, or



$$S<\begin{matrix}Bi-Se\\ \cdot\\ Bi-Se\end{matrix}>Pb$$

The crystals are trigonal with $a:c=1:1·226$. P. Groth and K. Mieleitner regarded it as a sulpho-salt related to zinckenite. The sp. gr. is 7·98, and the hardness 2–3. K. Johansson, and A. Schwantke described another mineral from Fahlun; it resembled molybdenum glance, and occurred in rhombic or monoclinic crystals with the composition $5PbS.3Bi_2(S,Se)_3$. It was called **wittite.** Its sp. gr. is 7·12; and its hardness 2–2·5. A mineral occurring in the dolomite of Serrania de Ronda was described by S. P. de Rubies, and named by C. Doelter, **rubiesite.** The composition is $8Bi_2S_3.Sb_2S_3.Bi_2(Te,Se)_3$. Its hardness is 2, and its sp. gr. 6·8.

According to W. von Bolton,[20] if an intimate mixture of eq. proportions of selenium and columbium is heated under fused potassium chloride, a black, brittle **columbium selenide** is formed; and similarly also with tantalum. The resulting black **tantalum selenide** is decomposed by exposure to air, forming hydrogen selenide.

The formation and properties of *sulphur selenide* are discussed in connection with selenium sulphide. No *tellurium selenide* has been prepared. According to J. J. Berzelius,[21] selenium and tellurium may be fused together in all proportions. Combination occurs with the evolution of heat to form an iron-black, brittle mass, with a crystalline fracture. The product fuses below a red-heat, and boils at a higher temp. It can be vaporized completely out of contact with air, but it readily oxidizes in air, forming what he regarded as tellurium selenite. H. B. Foullon pointed out that native tellurium often contains selenium; and E. S. Dana and H. L. Wells found that the *selentellurium* occurring in the Ojojama District, Honduras, has, after deducting gangue, 29·31 per cent. of selenium and 70·69 per cent. of tellurium. It occurs massive, with a hexagonal cleavage, and of a greyish-black colour. It is an isomorphous mixture of selenium and tellurium. According to G. Pellini and G. Vio, the two elements are completely isomorphous; the f.p.

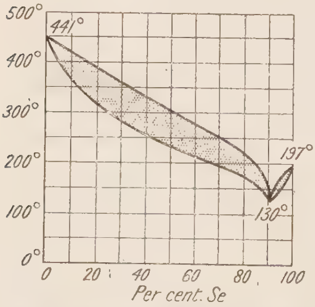


FIG. 46.—Freezing-point Curve of Mixtures of Selenium and Tellurium.

of mixtures of selenium and tellurium furnish a continuous curve between 219° and 450°, the f.p. of the respective elements. The upper portions of the solidified mixtures are richer in selenium than the lower ones. All the mixtures solidify in mixed crystals of the hexagonal-rhombohedral type, which is that to which the crystals of both selenium and tellurium belong. G. Pellini and G. Vio missed the minimum point of the curve, Fig. 46, given by Y. Kimata. Here the tellurium and selenium form two series of solid soln. These meet at 95 per cent. Se and 130°, at which temp. the liquid and solid phases have the same composition. The two branches of the liquidus and solidus curves intersect at a sharp angle, suggesting a eutectic, but all the alloys are microscopically homogeneous. Whether a compound is formed at this point is undetermined. M. Padoa found that the sp. hts. of solid soln. were additive—*vide* sp. ht. sulphur. There is no evidence to show whether or not a compound is formed. S. Lossana studied the ternary system: S–Se–Te—*vide* tellurium sulphide.

H. Moissan [22] obtained **chromium selenide,** CrSe, by heating chromous chloride in a stream of hydrogen selenide, or by heating chromium hemitriselenide in hydrogen. The black powder is readily attacked by chlorine. W. F. de Jong and H. W. V. Willems found that the X-radiogram of chromium monoselenide agrees with a hexagonal lattice having a=3·59 A., and c=5·80; and a sp. gr. 6·74. H. Moissan also obtained **chromium hemitriselenide,** Cr_2Se_3, by heating chromic chloride in a current of hydrogen selenide, or chromic oxide, which has not been pre-calcined, in selenium vapour carried along by hydrogen or nitrogen. The black crystalline, or brownish-black amorphous mass resembles chromic sulphide. It forms the monoselenide when heated out of contact with air; and it is with difficulty attacked by acids. L. Moser and K. Atynsky could not make chromium selenide by a wet process. J. Milbauer prepared **potassium chromic selenide,** $K_2Cr_2Se_4$, by heating a mixture of selenium, potassium cyanide, and chromium sesquioxide at a red-heat. The salt forms dark green, hexagonal crystals, which are readily soluble in nitric acid, but insoluble in hydrochloric acid.

H. Uelsmann [23] treated an acidified soln. of ammonium molybdate with hydrogen selenide and obtained a dark brown soln. which gives a brown precipitate of **molybdenum triselenide,** $MoSe_3$, when treated with acids. The product is contaminated with a bluish-grey substance. L. Moser and K. Atynsky made the triselenide by the action of molybdic salt on a soln. of hydrogen selenide. W. W. Coblentz found that molybdenum selenide is not photochemically sensitive. According to E. Wendehorst, if a sulphuric acid soln. of ammonium molybdate be reduced with zinc until it becomes deep reddish-brown, and then saturated with hydrogen selenide, dense, brownish-black leaflets of **molybdenum hemipentaselenide,** Mo_2Se_5, are deposited; and if a mixture of molybdenum trioxide and selenium be heated in hydrogen to dull redness, bluish-black, glistening leaflets of **molybdenum diselenide,** $MoSe_2$, are formed, and they are insoluble in alkali soln. V. M. Goldschmidt discussed the structure of the crystals. E. Wendehorst observed that when a mixture of potassium carbonate, selenium, and molybdenum dioxide is fused above 1200°, and the product is leached with water, dark lead-grey crystals of **molybdenum hemitriselenide,** Mo_2Se_3, remain. If a soln. of potassium molybdate in conc. potash-lye, be treated with hydrogen selenide, red needles of **potassium selenomolybdate,** K_2MoSe_4, separate; while if a soln. of molybdic acid in conc. aq. ammonia be similarly treated, **ammonium selenomolybdate,** $(NH_4)_2MoSe_4$, appears in glistening blue crystals; but **sodium selenomolybdate** could not be similarly obtained. All selenium compounds of molybdenum prepared in the wet way rapidly decompose on exposure to the air; their preparation must therefore be carried out in an atm. of nitrogen.

H. Uelsmann, and L. Moser and K. Atynsky prepared **tungsten triselenide,** WSe_3, by similar processes to those employed for the molybdenum compound, but using sodium tungstate in place of the molybdate. It is soluble in soln. of alkali hydroxides, sulphides, and selenides. When heated out of contact with air it loses one-third of its selenium, forming **tungsten diselenide,** WSe_2. V. M. Goldschmidt discussed the structure of the crystals. C. H. Weber claimed that traces of selenium makes tungsten filaments tougher and more flexible than the ordinary filaments used for incandescent lamps. According to V. Lenher and A. G. Frueman, a soln. of ammonium tungstate in a flask was treated with nitrogen to sweep out the air, and then with hydrogen selenide. If the soln. be sat. with gas, green crystals of **ammonium tetraselenotungstate,** $(NH_4)_2WSe_4$, were formed; and if the soln. is incompletely sat., red crystals of **ammonium dioxydiselenotungstate,** $(NH_4)_2WSe_2O_2$, are produced. These salts, when washed and dried, do not show any discoloration when kept in a calcium chloride desiccator for several months. However, a slight odour which resembles hydrogen selenide can be detected. Both the selenotungstate and the diseleno-tungstate are readily soluble in water, somewhat soluble in alcohol, but insoluble in ether, benzene, and carbon disulphide. The selenotungstate yields a red aq. soln. which is slowly decomposed in the air, giving a brown precipitate. The precipitate is probably a mixture of selenium and tungsten triselenide, WSe_4. The diseleno-tungstate gives an aq. soln. which is similar in colour to a soln. of potassium dichromate, but the colour of conc. soln. is also red. Aq. soln. of the diseleno-tungstate are slowly decomposed in the air and a precipitate of red selenium is formed. Green crystals of ammonium seleno-tungstate are reddish-brown in a finely pulverized state. In order to minimize oxidation, the crystals were pulverized under benzene.

A. Colani[24] prepared **uranium diselenide,** USe_2, by heating to dull redness sodium hexachlorouranate in hydrogen selenide, or better, in the vapour of selenium carried along in a current of hydrogen; if the temp. attains 1000°, crystals of **uranium hemitriselenide,** U_2Se_3, are formed. The diselenide is also formed by double decomposition of sodium hexachlorouranate and tin selenide at a red-heat in hydrogen. The black, crystalline powder of the diselenide may inflame spontaneously in air. It can be preserved in sealed tubes. Its properties resemble those of uranium disulphide, but it is far more sensitive towards oxidizing agents. L. Moser and K. Atynsky could not prepare uranium selenide by the wet process. J. Milbauer prepared **uranyl selenide,** UO_2Se, by heating a mixture of selenium, potassium cyanide, and uranium oxide (prepared from uranyl acetate) at low red-heat. The salt forms black, hexagonal prisms with a metallic lustre and closely resembling uranyl sulphide. When cold hydrochloric acid is added to it, hydrogen selenide is evolved and uranyl chloride produced. It is acted on very vigorously by nitric acid, selenium at first separating and then gradually oxidizing.

According to J. J. Berzelius,[25] soln. of manganese salts and alkali selenides give a pale red precipitate which becomes a darker red when exposed to air owing to its decomposition and the separation of selenium. E. Reeb compared its properties with those of the sulphide. C. Fabre, and H. Fonzes-Diacon obtained **manganese selenide,** MnSe, in a similar way. C. Fabre also prepared it by passing the vapour of selenium over red-hot manganese; L. Moser and K. Atynsky obtained it by the action of a manganese salt on a soln. of hydrogen selenide out of contact with air; and H. Fonzes-Diacon, by passing a mixture of hydrogen selenide and nitrogen over anhydrous manganous chloride at a dull red-heat, and by reducing manganese selenate with four times its weight of carbon in an electric furnace. Manganese selenide appears as a shining, grey regulus containing acicular crystals, and that prepared in the electric furnace consists of greyish-black, opaque, cubic crystals. W. F. de Jong and H. W. V. Willems found that the X-radiograms agree with a cubic lattice, and E. Broch gave for the face-centred cubic lattice, $a=5\cdot448$ A., and sp. gr. 5·47. H. Fonzes-Diacon observed that the sp. gr. is 5·59 at 15°. The compound is stable at a high temp. C. Fabre gave 31·14 Cals. for the heat of formation of the crystalline selenide, and 27·50 Cals. for that of the precipitated. According to H. Fonzes-Diacon, manganese selenide is completely oxidized when heated to redness in oxygen; it is attacked by boiling water; and hydrogen dioxide, acidified with hydrochloric acid, converts it into selenate. It is easily attacked by dil. acids—with hydrochloric acid, hydrogen selenide is evolved. It burns in chlorine to manganous chloride and selenium dichloride. J. Meyer and H. Bratke prepared **potassium manganese selenide** by fusing together potassium carbonate, manganese and selenium; it is unstable in air, and in contact with water or acids.

According to J. J. Berzelius,[26] when the vapour of selenium is passed over heated iron filings, the combination which occurs is attended by the evolution of light and heat; when a mixture of iron filings and powdered selenium is heated, the partial combination which occurs is not attended by visible combustion. The yellowish-grey iron selenide so formed has a metallic lustre, and it is a hard, brittle mass with a granular fracture. It fuses at a high temp., forming a brittle regulus with a conchoidal fracture. According to G. Tammann and K. Schaarwächter, the two elements begin to react at 200°. The selenide was also prepared by E. Divers and T. Shimidzu—*vide supra,* hydrogen selenide—and its analysis agreed with **ferrous selenide,** FeSe, or **iron monoselenide.** G. Little melted the mixed elements under borax. H. Fonzes-Diacon prepared it by the action of selenium vapour carried in a current of nitrogen, on red-hot iron; hydrogen selenide gives a similar result, but its action is slower. An impure product was also obtained by heating iron selenate with carbon. L. Moser and E. Doctor obtained ferrous selenide by passing selenium vapour over the metal heated in vacuo. Ferrous selenide forms a black, metallic mass which is stable in air. W. F. de Jong and H. W. V. Willems found that the X-radiograms agree with a hexagonal lattice having $a=3{\cdot}61$ A., and $c=5{\cdot}87$ A.; and a sp. gr. 6·78. I. Oftedal studied this subject. G. Little gave 6·38 for the sp. gr. C. Fabre obtained 18·44 Cals. for the heat of formation of the crystalline and 15·42 Cals. for the precipitated selenide. T. Midgley and C. A. Hochwalt used ferrous selenide as a catalyst for cracking petroleum oils. According to E. Reeb, hydrogen selenide gives a brownish-violet precipitate of hydrated ferrous selenide when passed into a soln. of a ferrous salt; with an acetic soln. of ferrous acetate, the precipitate is black. L. Moser and K. Atynsky obtained ferrous selenide by the action of a ferrous salt on a soln. of hydrogen selenide out of contact with air, but they could not prepare *ferric selenide,* Fe_2Se_3, in this way. E. Reeb found that ferric salt soln. are first reduced to ferrous salts by hydrogen selenide, and they then give the same precipitate. Hydrated ferrous selenide is insoluble in alkali-lye and soln. of ammonium sulphide, but it is soluble in hydrochloric, nitric, and acetic acids. Iron selenide, said J. J. Berzelius, dissolves in hydrochloric acid with the evolution of hydrogen selenide, and if air be present, a red cloud is formed owing to the decomposition of the hydrogen selenide to form selenium, and at the same time there is evolved another gas which has a disagreeable odour, is not absorbed by water or by alkali-lye, and gives a black precipitate with a soln. of mercurous nitrate. G. Little found that with dil. nitric acid it gives off hydrogen selenide, and it forms a yellow liquid with the conc. acid. J. J. Berzelius said that when powdered iron selenide is heated with selenium, it takes up more of the selenium, forming a brown powder—presumably from G. Little's analysis, **ferric selenide,** Fe_2Se_3, or **iron hemitriselenide**—which is insoluble in hydrochloric acid, and gives off the excess of selenium at a bright red-heat. G. Little obtained it as a yellowish-grey mass, by melting a mixture of selenium and iron selenide under borax; and H. Fonzes-Diacon, by the action of hydrogen selenide on ferric oxide or anhydrous ferric chloride at a dull red-heat. H. Fonzes-Diacon obtained **iron tritatetraselenide,** Fe_3Se_4—possibly from the analyses, Fe_7Se_8—by heating iron oxide to redness in a current of nitrogen charged with hydrogen selenide; **iron diselenide,** $FeSe_2$, by the action of hydrogen selenide on anhydrous ferric chloride at 250°–300°. W. F. de Jong and H. W. V. Willems could not prepare crystals of the diselenide. H. Fonzes-Diacon obtained **iron hemiselenide,** Fe_2Se, by heating to whiteness one of the above selenides in a current of hydrogen. According to H. Fonzes-Diacon, the iron selenides form oxide of iron and selenium dioxide when heated in oxygen: chlorine at a gentle heat displaces the selenium, and, at a higher temp., bromine, and iodine vapour act similarly at a higher temp. The iron selenides are attacked with difficulty by conc. hydrochloric acid, and by hydrogen chloride. Iron diselenide is not attacked at all by the acid. Hot fuming nitric acid transforms the selenides into selenites. J. Meyer and H. Bratke obtained **iron tritatetraselenide,** Fe_3Se_4, or $Fe[FeSe_2]_2$, by fusing together iron, selenium, and potassium cyanide; and **potassium iron diselenide,** $K[FeSe_2]$, in dark violet crystals, fairly stable in air, by fusing together iron, selenium, and potassium carbonate; and **silver iron selenide,** $3Ag_2Se.2Fe_3Se_4$, or $Ag_6Fe_6Se_{11}$, by fusing the appropriate elements together, but the products may really be a mixture.

J. J. Berzelius found that cobalt and selenium unite with incandescence when heated, forming a grey mass with a metallic lustre and crystalline structure, which fuses at a red-heat. G. Little used a similar process. If the combination is effected in an atm. of hydrogen, some hydrogen selenide is formed. The product is **cobalt selenide,** CoSe. If it be melted under borax, the selenide appears as a yellow crystalline mass of sp. gr. 7·647. H. Fonzes-Diacon also obtained it by passing the vapour of selenium over cobalt; and L. Moser and K. Atynsky, as in the case of ferrous selenide. W. F. de Jong and H. W. V. Willems found that the X-radiogram agrees with a hexagonal lattice with a=3·60 A., and c=5·27 A.; and a sp. gr. of 7·78. I. Oftedal studied this subject. C. Fabre gave 18·9 Cals. for the heat of formation of the crystalline selenide, and 15·2 Cals. for that precipitated by hydrogen selenide from soln. of cobalt salts. H. Fonzes-Diacon passed selenium vapour along with nitrogen over cobaltous chloride at a dull red-heat, and obtained microscopic, greyish-violet, octahedral crystals of **cobalt tritatetraselenide,** Co_3Se_4. Its sp. gr. is 6·54 at 15°, and it is isomorphous with linneite. By a similar process at a red-heat, grey **cobalt hemitriselenide,** Co_2Se_3, is formed; and below a red-heat, **cobalt diselenide,** $CoSe_2$. W. F. de Jong and H. W. V. Willems found that the X-radiogram of the regular pyritahedral crystals agree with a space-lattice with a=5·854 A., and a distance 2·41 A. between the Se and Co atoms. V. M. Goldschmidt discussed the structure of the crystals. H. Fonzes-Diacon observed that if any of these selenides be heated to whiteness in a current of hydrogen, **cobalt hemiselenide,** Co_2Se, is formed. If heated to whiteness in hydrogen, the selenium is slowly removed. When one of the selenides is heated in oxygen, cobalt oxide and selenium dioxide are formed; nascent hydrogen chloride slowly attacks the selenide; boiling fuming hydrochloric acid attacks it very little; and bromine-water with an excess of bromine dissolves it easily. J. Meyer and H. Bratke obtained **cobalt pentitahexaselenide,** Co_5Se_6, or $Co_3[CoSe_3]_2$ by fusing together a mixture of cobalt, selenium, and potassium cyanide. S. G. Gordon reported a lead-grey mineral from Colquechaca, Bolivia, which he named **penroseite.** Its composition corresponds with **cuprous lead cobalt selenide,** $Cu_2Se.PbSe.(Ni,Co)Se_2$, or $3CuSe.2PbSe_2.5(Ni,Co)Se_2$. It has a metallic lustre, and a radiating columnar structure, with the (001)-, (100)-, and the (010)-cleavages perfect; the prismatic (110)-cleavage is distinct; and the basal cleavage curved. The sp. gr. is 6·93, and the hardness 3. It is soluble in nitric acid. G. Frebold showed that *selenkobaltblei* is a mixture.

G. Little passed selenium vapour over heated nickel, and obtained **nickel selenide,** NiSe. H. Fonzes-Diacon carried the selenium vapour in a current of nitrogen over the nickel at a red-heat and obtained a similar product; and he also prepared it by passing the vapour of hydrogen selenide over nickelous chloride. L. Moser and K. Atynsky obtained it as in the case of ferrous selenide. H. Fonzes-Diacon said that the selenide is silver-white or grey, with a metallic lustre, brittle, and non-magnetic. The cubic crystals appear with tetrahedral twinning. N. Alsen found that the X-radiogram of nickel selenide, and its mixed crystals with ferrous sulphide, have the pyrrhotite structure.. When melted under borax nickel selenide furnishes a golden-yellow mass. W. F. de Jong and H. W. V. Willems found that the X-radiogram agrees with a hexagonal lattice having a=3·66 A., and c=5·33 A.; and a sp. gr. 7·41. I. Oftedal studied this subject. G. Little gave 8·46 for the sp. gr.; and H. Fonzes-Diacon, 5·453 at 15°. The selenide is stable in air, and melts at a bright red-heat, giving off a little selenium at the same time. C. Fabre gave 18·42 Cals. for the heat of formation of the crystalline selenide, and 14·8 Cals. for that which is precipitated when a nickel salt is treated with hydrogen selenide or sodium selenide. H. Fonzes-Diacon observed that when the selenide is heated in oxygen, nickel oxide and selenium dioxide are formed. Nickel selenide was found by G. Little to be insoluble in water. C. Fabre found that it is soluble in bromine and in bromine water. H. Fonzes-Diacon added that chlorine attacks it readily. G. Little said that it is insoluble in dil. or conc. hydrochloric acid; conc. boiling hydrochloric acid, added H. Fonzes-Diacon, acts only slowly, and hydrogen chloride at an elevated temp. slowly forms nickel chloride. G. Little found that the selenide is slowly dissolved by nitric acid; and readily dissolved by aqua regia. H. Fonzes-Diacon observed that nitric acid converts the selenide into selenite. According to H. Fonzes-Diacon, if anhydrous nickelous chloride be heated to dull redness in a current of hydrogen selenide, grey, cubic crystals of **nickel hemitriselenide,** Ni_2Se_3, or **nickel tritatetraselenide,** Ni_3Se_4, are formed; and if the action takes place at 300° with nickelous chloride or oxide, grey **nickel diselenide,** $NiSe_2$, is produced. According to W. F. de Jong and H. W. V. Willems, the X-radiograms of the pyritahedral, cubic crystals agree with a space-lattice having $a=6·022$ A., and a distance of 2·47 A. between the Ni and Se atoms. V. M. Goldschmidt discussed the structure of these crystals. H. Fonzes-Diacon observed that if one of the above described nickel selenides be heated to bright redness in a current of hydrogen, a golden mass of **nickel hemiselenide,** Ni_2Se, is formed. It slowly loses selenium if heated in hydrogen for a long time. J. Meyer and H. Bratke prepared **nickel pentitahexaselenide,** Ni_5Se_6, or $Ni_3[NiSe_3]_2$, by fusing a mixture of nickel, selenium, and potassium carbonate.

According to J. J. Berzelius,[27] when a mixture of selenium and palladium is heated, combination occurs and a **palladium selenide** is formed with the evolution of heat. The grey mass is infusible before the blowpipe, but gives off selenium, yielding a seleniferous, greyish-white, brittle, and crystalline button. F. Rössler obtained **palladium selenide,** PdSe, by heating a mixture of palladious amminochloride (10 grms.) and selenium (5 grms.) under borax. L. Moser and K. Atynsky prepared dark brown palladium selenide by the action of a palladious salt on a soln. of hydrogen selenide out of contact with air. L. Thomassen found that the crystals of the monoselenide are of the nickel arsenide type with $a=4·127$ A., and $c=5·663$ A. V. M. Goldschmidt discussed the subject. F. Rössler also obtained what he regarded as **palladium tetritaselenide,** Pd_4Se, from palladious amminochloride (60 grms.) and selenium (2 grms.). J. J. Berzelius obtained similar results with platinum as with palladium, and he added that the combination is attended by vivid incandescence. F. Rössler obtained **platinum selenide,** PtSe, by melting an intimate mixture of platinum powder and selenium under borax at 1050°–1100°. The dark grey, columnar crystalline mass is brittle, and can be fused before the blowpipe with the loss of selenium. H. Fonzes-Diacon obtained it by the action of hydrogen selenide on gently heated platinous chloride; and on platinous chloride suspended in water. He also prepared **platinum diselenide,** $PtSe_2$, by heating reduced platinum in a current of hydrogen selenide; by the action of hydrogen selenide on red-hot anhydrous platinic chloride, or on an aq. soln. of platinic chloride. L. Moser and K. Atynsky made it by the action of a platinic salt on a soln. of hydrogen selenide out of contact with air. A. Minozzi obtained it by heating the triselenide to dull redness in a current of carbon dioxide and by heating an intimate mixture of the two elements at a bright red-heat for 6 hrs. in a current of carbon dioxide. L. Thomassen prepared crystals of platinum diselenide which are of the cadmium iodide type, and the space-lattice has $a=3·724$ A., and $c=5·062$ A. A. Minozzi found that the grey powder has a sp. gr. 7·65; H. Fonzes-Diacon gave 6·426 at 15°. When heated in oxygen, it loses selenium at 250°, and at a higher temp. forms selenium dioxide and platinum. When gently heated in chlorine, the selenium is displaced. L. Pigeon said that the diselenide resists chlorine at 360°. L. Moser and K. Atynsky said that it readily forms complex salts with alkali sulphides and selenides. According to A. Minozzi, **platinum triselenide,** $PtSe_3$, is obtained as a black, flocculent precipitate by the action of formaldehyde on a soln. containing a platinichloride and a selenite in presence of excess of an alkali hydroxide, thus: $K_2PtCl_6+3SeO_2+8H.CHO+12KOH=PtSe_3+6KCl+8H.CO_2K+10H_2O$. The black powder has a sp. gr. of 7·15. At 140°, in air, it begins to form selenium dioxide, and in oxygen at 450°, it is converted into selenium tetrachloride; conc. hydrochloric acid has no action; hot conc. nitric or sulphuric acid have a limited action; it is slowly dissolved by aqua regia, and by chlorine water; it is insoluble in carbon disulphide. L. Thomassen observed that **osmium diselenide,** $OsSe_2$, has crystals of the pyrite type with a space-lattice having $a=5·933$ A., whilst a product of the composition of **osmium monoselenide,** OsSe, is a mixture of the diselenide and metal. Similarly with **ruthenium diselenide,** $RuSe_2$, the space-lattice is of the pyrites type, with $a=5·921$ A.; and the product with the composition **ruthenium monoselenide,** RuSe, is a mixture of the diselenide and metal. None of these compounds showed any evidence of ferromagnetism. V. M. Goldschmidt discussed the structure of these selenides. F. Fritzmann investigated some complex platinum and palladium organic selenium compounds.

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§ 8. Selenium Dioxide and the Lower Oxides

J. J. Berzelius [1] observed that selenium exhibits less affinity than sulphur for oxygen—*vide supra*, the action of air and oxygen on selenium—and F. Krafft and O. Steiner made a similar observation—the affinity of the elements of the sulphur family decreases as the at. wt. rises in the group, while the affinity for chlorine increases. J. J. Berzelius said that when selenium burns in air or oxygen, a mixture of **selenium monoxide,** SeO, and selenium dioxide is formed—if the selenium be burnt in a vessel filled with oxygen, and the selenium dioxide be removed by agitation with water, a mixture of oxygen and selenium monoxide remains in small quantities. When a mixture of selenium and selenium dioxide is heated the monoxide is formed, although the greater proportion of each sublimes unchanged; and when selenium sulphide is heated with a mixture of nitric and hydrochloric acid containing insufficient nitric acid completely to oxidize the selenium, the sulphur which remains unoxidized reduces the selenious acid. J. J. Berzelius described selenium monoxide as a colourless gas with an odour like that of a horse-radish, and so strong and penetrating that one-fiftieth of a grain is sufficient to fill a room with its odour. It does not redden litmus; it is slightly soluble in water to which it imparts its odour and taste; it is absorbed by alkali-lye only in proportion to the water present; and it is not precipitated from its aq. soln. by hydrogen sulphide. Thus far J. J. Berzelius. The source of the odour of burning selenium has been discussed in connection with the physiological action of selenium. C. Chabrié said that by heating selenium at 180° until its weight is constant there remains solid selenium monoxide. A. W. Peirce could not confirm this; rather did he obtain a loss in weight due to the volatilization of selenium. A mixture of selenium and selenium dioxide in a tube at a press. of 4 mm. was heated at 180° to 200° so that the contents of the tube vaporized and were maintained in a state of vapour for 7 hrs. No gas was found in the cooled tube, and the contents possessed no odour. V. Lenher observed that in subliming large quantities of selenium dioxide, no odour like that attributed by J. J. Berzelius to selenium monoxide was noticed; on heating a mixture of eq. quantities of selenium and its dioxide, either in an open vessel, or in a sealed tube, to the b.p. of selenium, no interaction took place, and no gaseous product could be detected. Selenium monobromide does not act on dry silver oxide below 20°, but at this temp. a violent action takes place and selenium dioxide alone is formed. V. Lenher concluded that selenium monoxide does not exist.

F. von Konek [2] said that when diantipyryl selenoselenide, $R_2Se : Se$, is burnt in oxygen in a bomb at 25 to 30 atm. press., a white, amorphous **selenium tritatetroxide,** Se_3O_4, is deposited on the walls of the containing vessel. This oxide is almost insoluble in water; it is decomposed by boiling soda-lye with the deposition of one-third of the selenium in a free state, and the remainder forms sodium selenium salts. Diantipyryl monoselenides and diselenides of the type R.Se.Se.R. give no trace of this oxide.

According to C. A. Cameron and J. Macallan, in the reaction between selenium trioxide and selenium in the cold, an intense green colour is developed; and a similar green colour was observed by G. Magnus to be imparted to sulphuric acid by the dissolution of selenium. The reaction was investigated by N. W. Fischer, and R. Weber. The last-named isolated $SeSO_3$; hence C. A. Cameron and J. Macallan inferred that in the case of selenium trioxide and selenium, **selenium hemitroxide,** Se_2O_3, or **selenium sesquioxide,** is the cause of the green coloration—*vide infra.* The green coloration may be due to colloidal selenium.

J. J. Berzelius [3] discussed **selenium dioxide,** SeO_2, during his observations of selenium. E. Bertrand observed some lead selenide covered with fine white needles of selenium dioxide, and he called the mineral *selenolite.* According to J. J. Berzelius, selenium can be sublimed in air without change; it takes fire only when strongly heated, and then burns to the dioxide. If selenium be heated in a glass tube until it boils, and oxygen gas be passed over it, combustion occurs, and selenium dioxide sublimes. Selenium dioxide is formed when selenium is dissolved in warm nitric acid or aqua regia, and the liquid heated in a retort. The acid liquor distils over first, and subsequently selenium dioxide sublimes. N. W. Fischer added that if aqua regia be employed a trace of selenic acid is formed at the same time. E. Wohlwill said that as soon as the acid liquor has distilled off, the contents of the retort may bubble up with explosive violence, but this was not observed by J. Thomsen, H. Topsöe, or F. Clausnizer, who employed this mode of preparation. J. Meyer prepared the dioxide in the following manner:

> Selenium in quantities of 60–75 grms. is heated to its m.p. in a porcelain boat placed in a wide, hard-glass tube; a very rapid current of oxygen which had been passed through fuming nitric acid is passed over it, causing the molten selenium to burn with a brilliant blue flame and to give a sublimate of selenium dioxide the purity of which increases with increasing rate of the supply of oxygen. The product, which contains small quantities of oxides of nitrogen, is purified by being sublimed in the same tube in a current of pure oxygen. To avoid loss of material, the tube is connected with a doubly tubulated vessel of two litres capacity in which the final traces of the dioxide are deposited. The combustion of 60–70 grms. of selenium can be effected in about one and a quarter hrs.

He added that the oxidation of selenium appears to be sensitive to catalytic influences, being accelerated by acidic substances—*e.g.* the vapour of nitric acid—

and retarded by alkaline substances—*e.g.* glass. J. J. Berzelius also observed the formation of selenium dioxide when selenium is similarly treated with sulphuric acid, or with a mixture of sulphuric acid and manganese dioxide. J. Thomsen obtained selenium dioxide of a high degree of purity by dissolving in water the dioxide prepared by the nitric acid process; treating the liquid with baryta-water, so as to precipitate any sulphate; evaporating the filtered liquid to dryness, and subliming. J. Jannek and J. Meyer said that it is impossible to prepare anhydrous selenium dioxide by the sublimation of the acid, and they preferred to oxidize selenium by heating it in a current of nitrogen peroxide. H. Moissan and P. Lebeau noticed that selenium dioxide is formed when the vapour of sulphuryl fluoride acts on selenium in a glass vessel: $2SO_2F_2+SiO_2+Se=SeO_2+2SO_2+SiF_4$.

The physical properties of selenium dioxide.—J. J. Berzelius said that selenium dioxide sublimes in white, four-sided needles with a peculiar lustre, or, if the sublimate is deposited in a hot place, it may form a dense, white, translucent mass. J. Meyer and M. Languer said that the crystals obtained from aq. and alkaline soln. are colourless; and that the vapour is yellowish-green. The crystals melted in a closed tube at 350° furnish an orange-yellow liquid, and a yellowish vapour. The colour is not due to selenium because dissociation does not occur. Selenium dioxide forms coloured soln. when dissolved in sulphuric or selenic acid. A. Weller showed that tellurium dioxide and tetrachloride are also examples of colourless substances giving coloured liquids and vapours. According to C. F. Rammelsberg, the **crystals** are monoclinic prisms with the axial ratios $a:b:c=1·292:1:1·67$, and $\beta=101°$. G. F. Hoffmann and V. Lenher found that the precipitated dioxide has a lower sp. gr. than the sublimed dioxide. F. Clausnizer found the **specific gravity** to be 3·9538 at 15·3°/15·3°; G. F. Hoffmann and V. Lenher gave 3·590 to 3·595 at 20°. E. Mitscherlich found the **vapour density** to be 4·03, when the theoretical value for SeO_2 is 3·849. E. B. R. Prideaux and G. Green found that the effect on the b.p. of ethyl alcohol indicates a **molecular weight** of 122·6, when the theoretical value for SeO_2 is 111·2. This corresponds approximately with a 10 per cent. association of the mols.; G. F. Hoffmann and V. Lenher found the mol. wt. in a soln. of selenyl chloride to correspond with $(SeO_2)_3$. H. M. Vernon inferred, from a comparison of the b.p. of related compounds, that the mol. of the solid is associated, $(SeO_2)_4$. E. B. R. Prideaux and G. Green found the mol. wt. of selenium dioxide in boiling ethyl alcohol to be 117·5. H. Remy discussed the structure of selenious acid. J. J. Berzelius said that under ordinary atm. press., selenium dioxide does not fuse when heated, but it merely sinters together; it vaporizes just below the b.p. of sulphuric acid, giving a vapour the colour of chlorine E. Cornec observed that the curve showing the lowering of the f.p. of selenious acid during its progressive neutralization with a soln. of potassium hydroxide has two breaks corresponding with the dibasicity of the acid; and similar results were obtained with sodium hydroxide. J. Jannek gave for the **vapour pressure,** p mm., of selenium dioxide:

	20°	70°	94°	181°	232°	299°	311°	315°	320°
p . . .	0·0	12·5	20·2	39·0	67·8	450·6	610·9	760·0	848·0

C. Chabrié added that the **melting point** is 340° if the dioxide be heated in a sealed tube in an atm. of dry air, and on cooling, it solidifies to a hard, white, crystalline mass. J. Thomsen gave for the **heat of formation** with crystalline selenium $(Se,O_2)=57·71$ Cals., and with vitreous selenium, 57·079 Cals. E. Petersen gave with amorphous selenium, soluble in carbon disulphide, 57·25 Cals.; with monoclinic selenium soluble in that menstruum, 56·20 Cals.; and with metallic selenium, insoluble in that menstruum, 55·82 Cals. E. Cornec found that the curve showing the change of the index of refraction of a soln. of selenious acid during its progressive neutralization with a soln. of sodium hydroxide has two breaks corresponding with the dibasicity of the acid; and similar results were obtained with aq. ammonia. J. Papish found that the vapour of selenium dioxide in the bunsen flame gives an intense blue colour; and elementary selenium is deposited on a cold plate held in the flame. D. Gernez found that the **absorption spectrum** of the vapour is continuous in the red, and has numerous lines in the blue and violet region.

The chemical properties of selenium dioxide.—J. J. Berzelius said that the vapour of selenium dioxide has a pungent, and sour smell, while the taste of the solid is acidic at first, and afterwards leaves a burning sensation. Selenium dioxide is not decomposed in the slightest degree by heat or light. According to J. J. Berzelius, and A. Klages, selenium dioxide is reduced when heated in **hydrogen.** For the action of **water,** *vide infra.* The dioxide attracts moisture from the air. According to A. Ditte, selenium dioxide rapidly absorbs dry **hydrogen fluoride,** forming oxyhydrofluorides (*q.v.*); and E. B. R. Prideaux and J. O'Neil Millott observed that $SeO_2.5HF$ is formed; dry **hydrogen chloride** forms oxyhydrochlorides (*q.v.*); dry **hydrogen bromide** forms oxyhydrobromides (*q.v.*); likewise **hydrogen iodide** forms oxyhydriodides (*q.v.*). C. A. Cameron and J. Macallan found that when distilled with **sodium chloride,** selenyl chloride is formed: $2SeO_2+2NaCl=Na_2SeO_3+SeOCl_2$. J. J. Berzelius said that selenium dioxide doubtless gives up its oxygen to **sulphur** when a mixture of the two is heated; and F. Krafft and O. Steiner observed that if the mixture is heated to the m.p. of selenium in an atm. of carbon dioxide, in a sealed tube, black selenium and liquid sulphur dioxide are formed. A. Ditte observed that **hydrogen sulphide** reacts with selenium dioxide, forming sulphur and selenium sulphide. Dry selenium dioxide cannot be reduced by **sulphur dioxide,** indeed, H. O. Schulze observed that selenium dioxide can be sublimed in an atm. of sulphur dioxide. R. Metzner found that selenium dioxide can be dissolved in monohydrated **sulphuric acid,** especially if warm, and when the hot soln. is cooled the dioxide is deposited again. F. W. O. de Coninck said that hot sulphuric acid converts selenium dioxide into $SeSO_3.H_2Se$, and amorphous, reddish-brown selenium—*vide infra,* selenium oxysulphides. V. Lenher and H. B. North said that **thionyl chloride** acts on selenium dioxide, producing tetrachloride and sulphur dioxide; there is no reaction with **sulphuryl chloride** even at a high temp., or great press. For the action of **selenium,** *vide supra,* selenium monoxide. C. A. Cameron and J. Macallan said that the dioxide dissolves in warm **selenic acid,** and most of it crystallizes out again on cooling without the formation of a thionic acid.

According to A. Michaelis, **ammonia** reacts with selenium dioxide evolving nitrogen with the separation of selenium; while C. A. Cameron and J. Macallan said that ammonia acts on a soln. of selenium dioxide in absolute alcohol, forming what they thought to be ammonium amide selenite, but which was shown to be ammonium ethyl selenite, $NH_4(C_2H_5)SeO_3$. F. W. O. de Coninck found that selenium dioxide yields nitrogen, and black, amorphous selenium when treated with **hydrazine:** $SeO_2+N_2H_4=N_2+Se+2H_2O$; and nitrogen and reddish-brown, amorphous selenium with **hydroxylamine** hydrochloride: $SeO_2+4NH_2OH=2N_2+Se+6H_2O$; A. Gutbier, and O. Hinsberg made a similar observation with respect to phenylhydrazine and hydroxylamine. F. W. O. de Coninck said that **nitric acid** converts selenium dioxide into selenic acid: $SeO_2+2HNO_3=H_2SeO_4+N_2O_4$; J. J. Berzelius said that selenium dioxide is reduced by **phosphorus.** By passing **phosphine** into an alcoholic soln. of selenium dioxide, C. A. Cameron obtained a pale yellow precipitate of phosphorus and selenium while a great proportion of the selenium remained in soln. as ethyl selenide, $(C_2H_5)_2Se$. F. W. O. de Coninck found that selenium dioxide is converted by **phosphorus pentachloride** into selenium tetrachloride and phosphoryl chloride: $SeO_2+2PCl_5=SeCl_4+2POCl_3$; and by **phosphorus trichloride** into brown, amorphous selenium and phosphoryl chloride: $SeO_2+2PCl_3=Se+2POCl_3$.

J. J. Berzelius said that selenium dioxide is doubtless reduced by **boron.** According to J. Papish, when selenium dioxide is introduced into the bunsen flame, an intense blue colour is produced, and selenium is deposited on a cold surface introduced into the blue flame. J. J. Berzelius found that the dioxide is reduced by **carbon,** and by organic substances. The dioxide is freely soluble in **ethyl alcohol.** F. W. O. de Coninck found that 100 parts of **methyl alcohol** at 11·8° dissolve 10·16 parts of selenium dioxide, and 100 parts of 93 per cent. ethyl alcohol at 14° dissolve 6·67 parts of the dioxide. O. Hinsberg found that when a soln. of selenium dioxide in 96 per cent. alcohol is evaporated over sulphuric acid, there remains a syrup which slowly loses water and alcohol, leaving a residue of selenium dioxide. If, however, an absolute alcoholic soln., of selenium dioxide is evaporated over calcium chloride, large, transparent, quadratic plates, having the composition $SeO_2.C_2H_2O$, are deposited; these crystals lose their alcohol over sulphuric acid. E. B. R. Prideaux and G. Green discussed the possibility of the reaction: $SeO_2+C_2H_5OH=SeO(OH)OC_2H_5$. F. W. O. de Coninck said that 100 parts of **acetone** at 15·3° dissolve 4·35 parts of selenium dioxide; and 100 parts of **acetic acid** at 13·9°, 1·11 parts. O. Hinsberg said that the dioxide dissolves freely in hot acetic acid containing water, and, on cooling the soln., selenious acid is deposited in crystals having the composition H_2SeO_3. It is only sparingly soluble in boiling **acetic anhydride,** from which it crystallizes unchanged, but when heated with acetic anhydride at 180°–200°, it is reduced to selenium, the anhydride being oxidized to carbon dioxide and other compounds. T. Gassmann obtained a complex $SO_2(C_2H_2O_4)_2$, by treatment with **oxalic acid.** F. Clausnizer observed that selenium dioxide is not soluble in purified **benzene,** but impure benzene becomes yellow and red owing to the dissolution and decomposition of the dioxide. C. Chabrié found that in the presence of aluminium chloride, selenium dioxide reacts with benzene. O. Hinsberg observed that selenium dioxide forms aniline selenite when an alcoholic soln. treated with an ethereal soln. of **aniline** and water is added; the dioxide does not react with **carbamide,** but it yields a selenium compound and phenyl disulphide when treated with **phenyl mercaptide;** and it reacts with **aromatic o-diamines.** When a mixture of **hydrogen cyanide,** selenium dioxide, and acetic anhydride is heated in a sealed tube at 100°, impure selenium cyanide, $SeCy_2$, is formed. F. Carnevali obtained addition products with **tetramethylammonium chloride,** namely, $SeO_2.2N(CH_3)_4Cl$, and with **tetraethylammonium chloride,** namely, $SeO_2.2N(C_2H_5)_4Cl$.

According to F. C. Mathers and F. V. Graham, **lead dioxide** and selenium dioxide form lead selenate, and the reaction proceeds satisfactorily at 100°

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§ 9. Hydrate of Selenium Dioxide—Selenious Acid

O. Hinsberg[1] observed that selenium dioxide is readily soluble in water ; and A. Étard represented the solubility, S, of the dioxide in grams per 100 grms. of soln. at $\theta°$ between $-3°$ and $36°$ by $S=45{\cdot}0+0{\cdot}7692\theta$; and later gave for selenious acid, S grms. H_2SeO_3 per 100 grms. of soln.

	−10°	0°	10°	20°	25°	40°	60°	90°
S	42·2	47·4	55·0	62·5	67·0	77·5	79·3	79·4

F. W. O. de Coninck found 37·45 grms. of the dioxide dissolved in 100 grms. of water at 11·3° ; 38·46 grms. at 14° ; and 39·37 grms. at 15·6°. W. Manchot and K. Ortner gave for the percentage solubility S grms. SeO_2 :

	−0·2°	−5·0°	−11·3°	−23·0°	−21°	1·17°	22·0°	42·0°	65·0°
S . .	0·99	21·83	40·65	**57·0**	58·0	68·32	72·52	77·5	82·5
Solid phase	Ice				$SeO_2.H_2O$				

The results are plotted in Fig. 47. There is a eutectic point at $-23°$ and 57 per cent. of SeO_2. The solid phase below this temp. is ice, and above this temp. **monohydrated selenium dioxide,** $SeO_2.H_2O$, or **selenious acid,** H_2SeO_3. This was the only hydrate formed under these conditions ; there was no sign of the formation of $(H_2SeO_3)_2$ indicated by A. Rosenheim and L. Krause. There is probably a maximum with 86·07 per cent. SeO_2 for the transition from the monohydrated to the anhydrous dioxide. The dotted portion of the curve, Fig. 47, could not be explored because of the separation of selenium from the soln. by the decomposition of selenious acid.

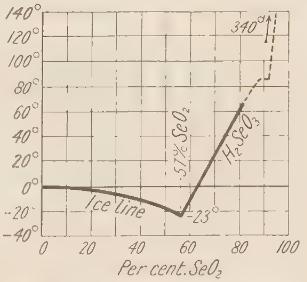

FIG. 47.—Solubility Curve of Selenium Dioxide in Water.

J. J. Berzelius observed that hydrated selenium dioxide crystallizes from hot aq. soln. in large crystals, when the soln. is slowly cooled, and in small grains when quickly cooled. The hydrate is also obtained by exposing the dioxide to air. R. Weber obtained the crystals by cooling a soln. of the dioxide in five times its weight of hot water. A. Michaelis evaporated the aq. soln. over sulphuric acid. Methods of F. Clausnizer, J. J. Berzelius, J. Thomsen, N. W. Fischer, etc., for preparing selenium dioxide (*q.v.*), involving the treatment of selenium with acids, were indicated in connection with that compound; and a soln. of selenious acid was first obtained, and this was subsequently dehydrated for the anhydride. C. Chabrié obtained selenious acid from a soln. of the dioxide in incompletely dried benzene; and O. Hinsberg, from a soln. of the dioxide in dil. acetic acid.

The analyses of R. Weber, and W. Manchot and K. Ortner agree with the formula H_2SeO_3. A. Rosenheim and L. Krause, and W. Manchot and K. Ortner found that the **molecular weight,** obtained from the depression of the f.p. of aq. soln., agrees with the formula H_2SeO_3; the results also indicated a slight association which has a tendency to decrease with time, and they found that the electrical conductivity indicated that the acid is associated to $(H_2SeO_3)_2$-molecules in aq. soln. No evidence of such an association was observed by W. Manchot and K. Ortner in freshly prepared aq. soln.

A. Michaelis and B. Landmann showed that while the alkyl iodides react with sulphites, forming sulphonic acids in agreement with the assumption that sulphurous acid may be regarded as a hydrosulphonic acid, $H.SO_2.OH$, yet selenious acid acts as an oxidizing agent with ethyl iodide and benzyl chloride; again, while sodium ethylate and thionyl chloride gave $SO(OC_2H_5)_2$, and ethyl iodide and silver sulphite gives $C_2H_5.SO_2.OC_2H_5$, yet the corresponding selenyl chloride forms in both cases $SeO(OC_2H_5)$, which is decomposed by water, forming selenious acid. This means that in all probability selenious acid is a true dihydroxylic acid, HO.SeO.OH. E. Divers and T. Shimidzu, however, assumed that the selenites have the asymmetric constitution. Although selenites are more basic than the sulphites, and selenium in general has a weaker affinity than sulphur, yet in spite of the many analogies between sulphites and selenites, the selenites, unlike the sulphites, may be dihydroxylic. They add that the iodide test employed by A. Michaelis and B. Landmann is not sufficient to establish the dihydroxylic character of the selenite, for it gives ambiguous testimony as to the constitution of the nitrites.

E. Divers and T. Shimidzu continue: Only silver selenite yields ethyl selenite; with potassium selenite it is difficult to get a reaction, and when this occurs, it leaves the selenium wholly deoxidized. Since ethylselenonic acid cannot be prepared by the oxidation method, it does seem allowable to group changes into a selenosic one, so as to enter into hydroxylic union with the ethyl. To suppose this is a way out of the difficulty is certainly much easier than it would be to consider metallic selenites as dihydroxylic salts. D. D. Karve found that applying the criteria for pseudo-acids, selenious acid alone and in conc. alcoholic soln. is an associated pseudo-acid, and aq. soln. contain a large proportion of the pseudo-acid, and only a small percentage of the hydrate of the true (monobasic) acid.

The physical properties of selenious acid.—J. Meyer and M. Langner observed that selenium dioxide melts to an orange-yellow liquid when heated and gives a yellowish-green vapour. The change is reversible and not attributable to dissociation into selenium and oxygen. Soln. of the oxide in warm, conc. sulphuric or selenic acid are distinctly yellow, but become lighter in colour when cooled. J. J. Berzelius described the **crystals** as being longitudinally striated similar to those of potassium nitrate; and R. Weber said that they are hexagonal prisms. F. Clausnizer gave 3·0066 for the **specific gravity** of the crystals at 15·3°/15·3°; G. F. Hoffmann and V. Lenher gave 3·004 at 15°/4°. F. W. O. de Coninck gave for the sp. gr. of aq. soln. between 13·0° and 15·6°, and containing the following percentage proportions of selenium dioxide:

SeO_2 . . .	1	2	4	5	6	8	10 per cent.
Sp. gr. . . .	0·9923	1·0068	1·0302	1·0346	1·0402	1·0571	1·0743

J. J. Berzelius said that when this hydrate is heated, it gives off water, and after that, selenium dioxide sublimes. F. Clausnizer found that when the clear crystals are confined over conc. sulphuric acid, they become opaque ; even after being kept 2 hrs. in the desiccator there is a marked loss in weight. This agrees with W. Manchot and K. Ortner's observations that the crystals cannot be dried without undergoing some dissociation : $H_2SeO_3 \rightleftharpoons H_2O + SeO_2$. F. Clausnizer observed that the crystals absorb moisture from humid air and appear to deliquesce more rapidly than crystals of selenium dioxide. R. Weber added that the crystals effloresce in dry air. W. Manchot and K. Ortner gave for the **vapour pressure,** p mm., of the crystals and of the sat. soln.—15° is here put for the temp. of the room :

		15°	32·0°	35·0°	35·4°	38·1°	38·3°	40·3°
p	Crystals . . .	2	—	4·5	—	6	—	7 mm.
	Sat. soln. . . .	—	16·5	—	18	—	19·5	22 mm.

A. Rosenheim and L. Krause observed for the **lowering of the freezing point,** θ, and the calculated mol. wt.—when the theoretical value is 129·2—for soln. containing w grms. of H_2SeO_3 per 100 grms. of water :

w	0·5810	1·8040	3·0900	4·6560	7·4480	10·5110
$\delta\theta$	0·09°	0·30°	0·52°	0·78°	1·17°	1·63°
Mol. wt. . .	112·7	113	113	113·3	121	122·5

There is here but a slight association of the mols. of the acid, which has a tendency to decrease with the ageing of the soln. The ionization also must be very slight indicating that selenious acid is a very weak one, and W. Manchot and K. Ortner calculated from their observations that the **degree of ionization** approximates to that of tartaric acid. They found for soln. of 1·253, 1·274, 13·420, and 13·750 grms. of H_2SeO_3 per 100 grms. of water the respective degree of ionization 0·21, 0·19, 0·03, and 0·04. Measurements of the mol. **raising of the boiling point** could not be made since selenious acid volatilizes with the steam. F. M. Raoult found the **mol. lowering of the freezing point** of selenious acid in aq. soln. to be 42·9—a number in the vicinity of the values found for selenic and sulphur acids. E. Cornec, on the other hand, obtained normal values between 19·2 and 21·5. J. Thomsen gave for the **heat of formation** of selenious acid, $(SeO_{2cryst.}, Aq.) = -0·920$ Cal. ; and $(Se, O_2, Aq.) = 56·336$ to 56·76 Cals. J. Jannek, and J. Meyer found the mol. heat of hydration of selenium dioxide is 3192 cals. The **heat of solution** of a mol of selenium dioxide in 400 mols of water is —0·920 Cal. ; and the **heat of neutralization,** $(SeO_{2aq.}, 2NaOH_{aq.}) = 27·02$ Cals. R. Metzner found that the **heat of oxidation** to selenic acid is comparatively small ; thus, $(SeO_{2solid}, O, H_2O) = 3·06$ Cals. M. S. Sherrill and E. F. Izard found that the equilibrium constants for the reactions $Cl_{2gas} + H_2SeO_3 + H_2O \rightleftharpoons 3H^{\cdot} + HSeO_4' + 2Cl'$, and $Br_2 + H_2SeO_3 + H_2O = 3H^{\cdot} + HSeO_4' + 2Br'$ at 25° were respectively $1·42 \times 10^9$ and 0·88. The reduction potential of $H_2SeO_3 + H_2O_{liquid} = 3H^{\cdot} + HSeO_4' + 2E$ was calculated to be —1·088 volts ; and the **free energy** at 25° of $Se_{solid} + 2O_{2gas} + H_{2gas} = H^{\cdot} + HSeO_4'$ to be —107,710 cals.

F. W. O. de Coninck said that when aq. soln. of selenious acid are exposed to **light,** reddish-brown, amorphous selenium, insoluble in carbon disulphide, separates out. J. H. Gladstone and W. Hibbert found that when the soln. is dil. from a conc. of 30·6 to one of 23·0 per cent. H_2SeO_3, the **molecular refraction** decreases from 26·98 to 26·84. E. Cornec found the **index of refraction,** μ, of a soln. of a mol of selenious acid in a litre of water at 19° to be 1·3462 ; and H. W. Stone found for aq. soln. of selenious acid containing p per cent. of H_2SeO_3, at 20° for the D-line, to be :

p . . .	0	1	5	10	20	30	40	50	52
μ . . .	1·330	1·3340	1·3382	1·3441	1·3570	1·4280	1·4570	1·4932	1·5010

F. Urban and V. W. Meloche gave a table for indicating the conc. of soln. of the acid from refractometer readings. P. Pringsheim and M. Yost studied the **Raman effect.**

A. Rosenheim and L. Krause measured the **H-ion concentration** of selenious acid and found for M-H_2SeO_3, $[H^{\cdot}]=6\cdot3\times10^{-3}$; for $0\cdot1M$-H_2SeO_3, $[H^{\cdot}]=7\cdot94\times10^{-3}$; and for $0\cdot01M$-H_2SeO_3, $[H^{\cdot}]=1\cdot995\times10^{-3}$. Hence it follows that the first **ionization constant** $K_1=4\cdot85\times10^{-3}$. The values of K calculated from conductivity data are indicated below. From their observations on the $H^{\cdot}$-ion conc., illustrated in Fig. 48, J. S. Willcox and E. B. R. Prideaux calculated for the first and second ionization constants of selenious acid $K_1=4\cdot0\times10^{-3}$, and $K_2=0\cdot87\times10^{-8}$; E. Blanc gave $K_1=2\times10^{-3}$, and $K_2=5\times10^{-8}$; and W. Ostwald gave $K_1=1\cdot59\times10^{-3}$. A. Rosenheim and L. Krause, and J. S. Willcox and E. B. R. Prideaux observed that selenious acid can be accurately titrated with soln. of sodium hydroxide using p-nitrophenol indicator as far as $NaHSeO_3$, and thymolphthalein, as indicator for complete neutralization although the end-point is not so sharply indicated. J. S. Willcox and E. B. R. Prideaux added that cochineal, lacmoid, and resazurin ought to be suitable for the first end-point. A. Rosenheim and L. Krause found that the mol. **electrical conductivities,** μ, of soln. of selenious acid containing a mol of the acid in v litres of water at 25°, are:

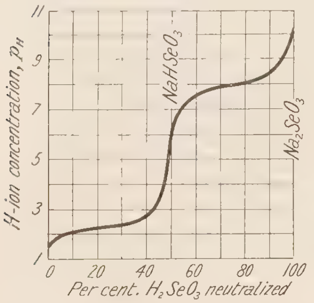

FIG. 48.—The $H^{\cdot}$-ion Concentration during the Neutralization of Selenious Acid with Sodium Hydroxide.

v . . .	32	64	128	256	512	1024	2048
μ . . .	91·6	120	144·2	192·05	233·6	276	322·8
K . . .	0·00343	0·00352	0·00281	0·00343	0·00368	—	—

H. F. Schott and co-workers calculated the reduction potential $Se_{black}+3H_2O_{liquid}=H_2SeO_3+4H^{\cdot}+4\ominus$ to be $-0\cdot740$ volt. The corresponding free energies, at 25°, are $-101\cdot36$ Cals. for H_2SeO_3; $-97\cdot85$ Cals. for $HSeO_3'$; and $-87\cdot89$ Cals. for SeO_3''. According to C. Manuelli and G. Lazzarini, in the **electrolysis** of a soln. of selenious acid, the acid is simultaneously reduced to selenium and oxidized to selenic acid: $H_2SeO_3+2H_2=3H_2O+Se$, and $2H_2SeO_3+2O=2H_2SeO_4$. Selenic acid may be conveniently prepared in this way, since the electrolysis gives rise neither to intermediate reduction products nor to complex acids, as is the case when sulphurous acid is electrolyzed. Theoretically, 0·7388 grm. of selenium should be separated at the cathode per ampere-hour, whilst at the anode a quantity of selenious acid corresponding with 1·4776 grm. of selenium should be oxidized. The diminution of the conc. of selenious acid and increase of the conc. of selenic acid are accompanied by a fall in the current yield both of selenium and selenic acid. When a large anode and consequently a small anodic current density is employed, the yield of the oxidation product is large, whilst with a large cathode a high yield of selenium is obtained. The diminished yield of selenic acid obtained when the quantity of this acid increases is not due to the establishment of an equilibrium between the oxidation of the selenious acid and the reduction of the selenic acid, since in the electrolysis of the latter, only a small amount of reduction occurs. The yields at 54° to 58° are not markedly different from those at 25°—*vide infra,* preparation of selenic acid for the electro-oxidation of selenious acid. G. Gore said that selenious acid is an exception to the rule that acids in contact with heated plates of platinum, palladium, or gold are thermopositive. A. Simek and H. Kadlcova did not observe the electrokinetic phenomenon, shown by tellurium dioxide, in their study of the electrocapillarity of selenium dioxide.

The chemical properties of selenious acid.—In general, oxidizing agents transform selenious acid into selenic acid, and reducing agents yield selenium. Only the stronger oxidizing agents effect the conversion, because, added R. Metzner, the heat of oxidation of selenious acid is small. According to C. Chabrié, **hydrogen** reduces selenious acid only when it is *in statu nascendi*. J. J. Berzelius observed that when iron or zinc is introduced into selenious acid, mixed with hydrochloric acid, selenium separates as a dark copper-red film on the metal, or in reddish-brown, or greyish-black flakes, according to the temp. In the case of iron, some iron selenide is formed. Acids other than hydrochloric acid may be used. If sulphuric acid be present, the deposition of selenium is very slow, and the selenium is contaminated with sulphur, while if arsenious acid be present, the precipitation of selenium is extremely slow. N. W. Fischer said that all the metals in the electrochemical series from zinc to silver—hence gold, palladium, and platinum are excluded—precipitate selenium from a mixture of selenious and sulphuric acids. Silver becomes covered with a film of silver selenide so that its surface assumes a yellow and brown tint, and this even when the liquid contains only one part of selenium in 20,000 to 50,000 parts of liquid. H. Reinsch made similar observations with respect to silver and copper in soln. of selenious and hydrochloric acids.

A. Mailfert observed that **ozone** oxidizes selenious to selenic acid; R. Metzner, and J. Meyer and K. Heider observed that a similar result is produced by **hydrogen dioxide**; J. Meyer and K. Heider, **sodium dioxide**; H. Rose, and H. Topsöe, **chlorine** or chlorine-water; K. H. Butler and D. McIntosh found that selenium dioxide is insoluble in liquid chlorine and has no effect on its b.p. J. Thomsen found that the dioxide is oxidized by **bromine.** S. R. Carter and N. J. L. Megson observed no complex formation with **hydrogen chloride**—*vide infra*, oxyhalogen salts. A. J. Balard found that the dioxide is oxidized by **hypochlorous acid**; J. Meyer and H. Moldenhauer, by **chloric acid**; and P. L. Blumenthal, by **potassium bromate,** and nitric acid. A. Ditte observed that **hydrogen fluoride** is energetically absorbed by selenium dioxide; J. J. Berzelius said that selenious acid is not decomposed in the slightest degree by **hydrochloric acid**; but B. Rathke showed that when a mixture of the two acids is evaporated a little selenium is volatilized as selenium chloride, hence, in analytical work, evaporations with hydrochloric acid or aqua regia should be avoided. A. W. Peirce, W. Muthmann and J. Schäfer, F. A. Gooch and W. G. Reynolds, and J. Meyer and W. von Garn, showed that selenious acid is reduced to selenium by **hydriodic acid,** and iodine is separated. H. F. Schott and co-workers found that the equilibrium constant, K, for the reaction $Se_{black}+2I_{2solid}+3H_2O=H_2SeO_3+4H^{\cdot}+4I'$, at 25°, is $K=[H_2SeO_3][H^{\cdot}]^4[I']^4$; or $K=1\cdot46\times10^{-14}$, when concentrations are expressed in mols per 1000 grms. of water.

Very cold, dil. soln. of selenious acid, when treated with **hydrogen sulphide,** were shown by J. J. Berzelius, H. Rose, B. Rathke, A. Ditte, A. Bettendorf and G. vom Rath, E. von Gerichten, and E. Divers and T. Shimidzu to yield a precipitate containing sulphur and selenium in the at. proportion 2 : 1; in warm soln., the precipitate becomes plastic and red—*vide infra*, selenium sulphides. The reaction is represented: $H_2SeO_3+2H_2S=2S+Se+3H_2O$. E. Divers and T. Shimidzu showed that if the soln. is warm, sulphuric acid is formed and the precipitate contains a smaller proportion of sulphur: $4H_2SeO_3+2H_2S=2H_2SO_4+4Se+4H_2O$. This means that a hot soln. of selenious acid oxidizes not only the hydrogen but also the sulphur of hydrogen sulphide. Only in very cold soln. is the hydrogen alone oxidized; with hot soln., the sulphur is also oxidized. H. Rose added that the complete decomposition of selenious acid by hydrogen sulphide is as difficult as that of arsenic acid by the same reagent. The reaction was also studied by A. Gutbier and J. Lohmann. According to J. J. Berzelius, when **sulphurous acid,** or an alkali sulphite, is gradually added to selenious acid, mixed with hydrochloric acid, selenium is precipitated in red or reddish-brown flakes, at low temp., and in the dark; but when aided by heat, or exposed to direct sunlight, the action is first: $H_2SeO_3+2H_2SO_3=2H_2SO_4+Se+H_2O$. He continued: the precipitation is not completed with less than half-an-hour's boiling; and if nitric acid be present, the selenium is not all precipitated until the nitric acid has been decomposed by the addition of the necessary quantity of sulphurous acid. L. M. Clark gives $3H_2SO_3 + H_2SeO_3 = H_2Se + 3H_2SO_4$, and $2H_2Se + SeO_2 = 2H_2O + 3Se$. H. O. Schulze showed that the presence of hydrochloric acid is not essential because aq. soln. are reduced by sulphurous acid—*vide supra*, analytical reactions of selenium. The selenium with dil. soln. is in the colloidal state. The reaction is accompanied by the liberation of 71 Cals., $2(SO_2,Aq.,O) - (Se,O_2,Aq.) = (2 \times 63{\cdot}63 — 56{\cdot}16)$ Cals. The reaction is discussed below in connection with the selenothionic acids prepared by L. Marino and V. Squintani.

According to H. Rose, **ammonium thiosulphate** precipitates only a trace of sulphuriferous selenium in cold soln.; but with hot soln., more is precipitated; and if hydrochloric acid is present, still more: $H_2SeO_3 + 2(NH_4)_2S_2O_3 = 2S + Se + 2(NH_4)_2SO_4 + H_2O$. J. F. Norris and H. Fay represented the reaction between a soln. of **sodium thiosulphate** and selenium dioxide: $SeO_2 + 4Na_2S_2O_3 = 2Na_2S_4O_6 + Se + 2Na_2O$; in conc. soln., selenium is precipitated, and the soln. becomes alkaline, but in dil. soln. no selenium is precipitated, and the reaction is not complete according to this equation, owing to the sodium hydroxide formed neutralizing part of the selenious acid, which, therefore, does not enter into reaction. In the presence of hydrochloric acid, the reaction occurs according to the equation: $SeO_2 + 4Na_2S_2O_3 + 4HCl = Na_2S_4SeO_6 + Na_2S_4O_6 + 4NaCl + 2H_2O$. No selenium is precipitated, but sodium selenotetrathionate is formed, which cannot be isolated. The reaction is discussed below in connection with the selenothionic acids. O. Brunck, and J. Meyer and J. Jannek showed that red selenium is produced when selenious acid is reduced by **sodium hyposulphite.** J. J. Berzelius found that selenious acid is very little changed when boiled with **selenium,** only a small proportion is converted into selenious oxide—*vide supra*, analytical reactions of selenium. G. Gore found that the acid is insoluble in liquid **ammonia.** The reduction of selenious acid to selenium by **hydroxylamine** salts and by **hydrazine** salts was observed by C. Alexi, G. Pellini and co-workers, J. Jannek, and P. Jannasch and M. Müller; by **hypophosphorous acid,** observed by A. Gutbier and E. Rohn; and by **phosphorous acid,** observed by H. Rose, C. Alexi, and A. Gutbier, has been discussed in connection with the analytical reactions of selenium.

A. Jouve found that **acetylene** gives a red coloration with selenious acid in sulphuric acid soln., a reaction sensitive to the presence of 0·001 per cent. of selenium. A. Michaelis and B. Landmann's observations on the action of ethyl iodide and benzyl chloride have been previously indicated. Many **organic substances** act as reducing agents in hot or cold soln. V. E. Levine discussed the colour reactions with **phenol.** F. W. O. de Coninck and E. Chauvenet found that colloidal selenium is precipitated from soln. of selenious acid by glucose, lævulose, dextrose formaldehyde, paraldehyde, oenanthol, formic acid, acetic acid, oxalic acid, malonic acid, succinic acid, and pyroracemic acids. G. Lunge found that diphenylamine reduces selenious acid. S. A. Fokin studied the action of selenious acid on various unsaturated aliphatic acids; L. Marino and co-workers, on piperidine; and O. Hinsberg, on naphthalene diamine. M. P. Sergéeff, N. A. Orloff, E. Schmidt, J. G. Dragendorff, and P. Mecke found that a soln. of selenious acid in sulphuric acid gives characteristic colorations with **alkaloids**—codeine, morphine, etc. C. L. Jackson, A. Michaelis and F. Kunckell, E. von Gerichten, and B. Rathke studied organic compounds in which selenium takes the place of sulphur. C. Chabrié also found that selenious acid is reduced to selenium by alcohol fermentation. L. Marino and co-workers obtained a complex with piperidine, $SeO_2.C_5H_5N$. H. Brenek found that selenious acid yields two selenites with **titanium dioxide.** The action with various other oxides is discussed in connection with the selenites. Selenious acid in acidic soln. is oxidized by potassium permanganate—*cf.* selenic acid—and the reaction: $4SeO_2 + 2KMnO_4 = 3SeO_3 + K_2SeO_4 + Mn_2O_3$, has been applied to analytical work by F. A. Gooch and

E. W. Danner, B. Brauner, F. A. Gooch and C. F. Clemons, P. Lougier, R. Metzner, and W. T. Schrenk and B. L. Browning.

H. Reinsch observed that when metallic **copper** is placed in a warm soln. of selenious acid containing hydrochloric acid, it immediately becomes coated black; if the soln. remains long in contact with the copper, it turns light red from the separation of selenium. L. M. Clark found that the composition of the precipitate obtained by the reduction of selenious acid by sulphurous acid in the presence of copper sulphate and hydrochloric acid varies from that of cuprous selenide in slightly acid soln. to that of pure selenium in soln. containing much hydrochloric acid. It is suggested that the selenious acid is under all conditions first reduced to selenium: $SeO_2+2Cu_2Cl_2+4HCl=Se+4CuCl_2+2H_2O$, which subsequently affords cuprous selenide: $Se+2Cu_2Cl_2=Cu_2Se+2CuCl_2$. The extent of the formation of cuprous selenide depends on the hydrogen-ion conc. of the soln.

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§ 10. The Selenites

Selenious acid acts as a dibasic acid, forming a series of normal salts or *selenites* of the type M_2SeO_3, and a series of acid salts or *hydroselenites* of the type $MHSO_3$; and there are also salts of even higher acidity, $MHSO_3.H_2SO_3$, or $MH_3Se_2O_6$. In addition, there are *pyroselenites* of the type $M_2Se_2O_5$. There are also *complex salts*, or *heteropoly-salts* with molybdic acid, uranic acid, and vanadic acid.

J. J. Berzelius,[1] L. F. Nilson, and J. S. Muspratt obtained normal **ammonium selenite,** $(NH_4)_2SeO_3$, by dissolving selenious acid in a slight excess of conc. aq. ammonia, and leaving the soln. to evaporate in a warm place. If the temp. rises too high during the admixture, some selenium may be reduced. F. A. Flückiger observed that this salt is formed along with ammonium selenide when selenium and aq. ammonia are heated in a sealed tube. L. F. Nilson's analysis showed that the crystals are probably the *monohydrate*, $(NH_4)_2SeO_3.H_2O$, and he added that there is probably a higher hydrate still. J. J. Berzelius described the crystals as four-sided prisms, oblique four-sided plates, and feathery crystallites ; L. F. Nilson, as small white needles which, in contact with the mother-liquid, form transparent prisms. J. J. Berzelius, and J. S. Muspratt said that the salt deliquesces in air ; and L. F. Nilson, that when exposed to air, the normal salt loses ammonia and forms the hydroselenite. J. J. Berzelius, and J. S. Muspratt found that when the normal selenite is heated, it swells up giving off water and ammonia, and afterwards water and nitrogen together with a quantity of trihydrodiselenite partly dissolved in the water and partly as a sublimate ; selenium remains as a residue : $3(NH_4)_2SeO_3 = 9H_2O + 2NH_3 + 3Se + 2N_2$. R. Weinland and J. Alfa evaporated a conc. soln. of ammonium selenite in an excess of 40 per cent. hydrofluoric acid and found that some hydroxyl radicles are replaced by fluorine to form $SeO(OH).F(ONH_4)$. P. Lafon observed that of the alkaloids and glucosides tried, only morphine, and codeine gave a green coloration which gradually becomes brown. When a soln. of the normal salt in water is allowed to evaporate spontaneously, J. J. Berzelius found that ammonia is evolved and acicular crystals of **ammonium hydroselenite,** NH_4HSeO_3, are formed. They are stable in air. L. F. Nilson obtained the salt in hygroscopic prisms. E. Cornec measured the conductivity of soln. obtained by mixing different proportions of soln. of $\frac{1}{8}M$-, $\frac{1}{16}M$-, $\frac{1}{32}M$-, $\frac{1}{64}M$-, and $\frac{1}{128}M$-soln. of aq. ammonia and selenious acid. When the curves showing the product of the electrical conductivity and the sp. vol. of the soln. as a function of the proportion of the constituent soln. mixed together are plotted, there is a minimum corresponding with the hydroselenite for the three most conc. soln. ; and in all cases there is a maximum corresponding with the normal selenite, Fig. 49. There is no evidence of any other compound as suggested by the results of A. Miolati and E. Mascetti. E. Cornec measured the indices of refraction of mixtures of $2N$-H_2SeO_3- and N-NH_3-soln. at 10°, and found there is a linear fall from 1·3462 with 100 per cent.

of the selenious acid soln. to 1·3423 with 50 per cent. of the alkali soln. added. There is then a fall to 1·3422, 1·3421 with 66·6 per cent. of ammonia soln. and then a drop to 1·3379 with 100 per cent. of ammonia soln. L. F. Nilson reported deliquescent prisms of **ammonium dihydrotriselenite,** $2(NH_4)_2SeO_3.H_2SeO_3$, to be formed by evaporating a soln. of selenious acid in aq. ammonia. J. J. Berzelius obtained **ammonium trihydrodiselenite,** $(NH_4)HSeO_3.H_2SeO_3$, as a deliquescent mass, by evaporating a soln. of the hydroselenite, aided by heat or by treating it with an acid. He could not crystallize the salt; but L. F. Nilson obtained it in deliquescent prisms by evaporating the conc. soln. in vacuo. It loses ammonia when dried in vacuo over sulphuric acid. J. Jannek and J. Meyer said that a mixture of a conc. soln. of hydrazine hydrate and selenious acid yields a red soln. containing **hydrazonium selenite** and polyselenides, which, on dilution, forms a stable soln. of selenium.

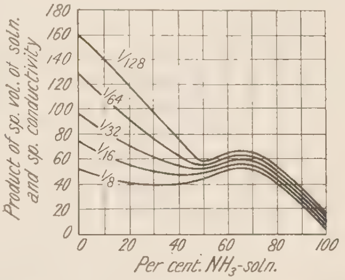


FIG. 49.—Progressive Addition of Ammonia to Solutions of Selenious Acid.

The alkali selenites were prepared by J. J. Berzelius by evaporating a soln. of the alkali carbonate sat. with selenious acid; and L. F. Nilson obtained monohydrated **lithium selenite,** $Li_2SeO_3.H_2O$, from a soln. of selenious acid in lithium hydroxide at 60°. The salt furnishes acicular crystals which lose half their water at 100°. A. Rosenheim and L. Krause's analysis agreed with the *tetritatrihydrate,* $4Li_2SeO_3.3H_2O$, not the monohydrate. J. J. Berzelius said that lithium selenite is hygroscopic; and it fuses below a red-heat, forming a yellow liquid which, on cooling, solidifies to a clear, pearly mass with a broadly foliated crystalline texture. A. Rosenheim and L. Krause found that 100 grms. of sat. aq. soln. contain

	0°	25°	47·5°	60°	100°
Li_2SeO_3	19·99	16·76	14·53	12·75	9·05 grms.

so that the solubility of lithium selenite like that of many other lithium salts, has a negative temp. coeff. Lithium selenite shows no tendency to adsorb lithium hydroxide from aq. soln.

L. F. Nilson prepared **sodium selenite,** Na_2SeO_3, by exposing the hydrated salt in dry air; and by evaporating an aq. soln., between 60° and 100°, of a mixture of sodium hydroxide and selenious acid, in eq. proportions; J. B. Krak used the same method; and C. A. Cameron and J. Macallan, by heating together a mixture of sodium chloride and selenium dioxide. The salt was also prepared by J. S. Muspratt—probably from an acidic soln. J. J. Berzelius said that the salt obtained by evaporating the aq. soln. in vacuo forms small grains; J. S. Muspratt obtained it in radiating crystals, which, according to L. F. Nilson, are tetragonal prisms. J. S. Muspratt said that the crystals can be fused without decomposition; J. J. Berzelius added that the salt is permanent in air; tastes like borax; is freely soluble in water, and insoluble in alcohol; N. R. Dhar found that the reduction by organic acids is promoted by the presence of oxidizing agents—potassium permanganate, or persulphate, hydrogen dioxide, manganese dioxide, potassium nitrite, etc. L. F. Nilson said that if the aq. soln. be evaporated at ordinary temp. it furnishes a syrupy liquid which deposits tufts of microscopic, acicular crystals, or four-sided prisms with the ends cut off obliquely. The crystals are the *pentahydrate,* $Na_2SeO_3.5H_2O$, which loses its water of crystallization in dry air. E. Cornec found the mol. lowering of the f.p. of water with normal sodium selenite is 43·2 to 49·4. A. Miolati and E. Mascetti observed the sp. conductivity of selenious acid when successive portions of a soln. of sodium hydroxide are added—*vide* Fig. 49—and the results indicate the existence of the trihydrodiselenite and hydroselenite. They found the mol. conductivity, μ, of soln. of a mol of sodium selenite and of sodium hydroselenite in v litres of water, to be:

	v	32	64	128	256	512	1024	∞
μ	Na_2SeO_3	85·87	92·45	96·35	99·44	102·9	105·0	112·6
	$NaHSeO_3$	79·42	84·15	89·52	92·91	96·71	100·5	106·0

The results agree with the dibasicity of the acid. E. Blanc found the degree of hydrolysis of a 0·0108N-soln. of sodium selenite to be 0·379 per cent. J. J. Berzelius said that **sodium hydroselenite,** $NaHSO_3$, is obtained in tufts of needle-like crystals by slowly cooling a syrupy soln. of the salt; and L. F. Nilson, by evaporating over conc. sulphuric acid a soln. of a mol of sodium carbonate with 2 mols of selenious acid. It forms radiating, monoclinic prisms; it is permanent in ordinary and in dry air, and at 100°; it does not fuse at 100°; and is freely soluble in water. J. S. Muspratt thought the salt was monohydrated, but L. F. Nilson said that it is not so. F. Sacc neutralized selenious acid with sodium carbonate; evaporated the soln. to a syrupy consistency; and left it to stand in vacuo. He said that crystals with the composition $2Na_2O.3SeO_2$ are formed; but this has not been verified. E. Cornec measured the indices of refraction of mixed soln. of $2N$-H_2SeO_3 and N-HaOH at 190°, and found that the index of refraction falls linearly from 1·3462 with 100 per cent. of the acid soln. to 1·3421 with 50 per cent. of the alkali soln., and it then rises linearly to 1·3432 with 100 per cent. of the alkali soln. E. Cornec found the mol. lowering of water with sodium hydrosulphite is 32·9 to 36·2, and if the salt be regarded as pyroselenite, the mol. lowering is 65·8 to 72·3. J. J. Berzelius said that **sodium trihydrodiselenite,** $NaH_3(SeO_3)_2$, is formed by the spontaneous evaporation of the aq. soln. L. F. Nilson used a soln. of a mol of sodium carbonate and 4 mols of selenious acid. J. S. Muspratt said that the salt is hemihydrated, but L. F. Nilson could not verify this. It furnishes monoclinic prisms which are permanent in ordinary and in dry air, but the salt has a tendency to effloresce.

J. J. Berzelius, J. S. Muspratt, and L. F. Nilson prepared **potassium selenite,** K_2SeO_3, and the last-named said that the *monohydrate*, $K_2SeO_3.H_2O$, is obtained by boiling a soln. of equimolar parts of potassium carbonate and selenious acid to remove the carbon dioxide, and allowing the soln. to evaporate at ordinary temp. over sulphuric acid. The salt is so deliquescent that the crystals could not be freed from the mother-liquor by squeezing between bibulous paper. L. F. Nilson said that the laminar, four-sided prisms are probably rhombic. J. J. Berzelius said that the salt melts when heated, forming a yellow liquid which becomes a white when it is solidified and cold. J. S. Muspratt said that the aq. soln. is alkaline, and added that the salt has an unpleasant taste, and it is soluble in all proportions in water, but not in alcohol, which precipitates it as an oily liquid from its aq. soln. J. J. Berzelius said that the salt is not soluble in alcohol. J. J. Berzelius, J. S. Muspratt, and L. F. Nilson prepared **potassium hydroselenite,** $KHSeO_3$, by the method used for the sodium salt. It furnishes laminar, four-sided, probably rhombic, prisms. The salt is very deliquescent, and is slightly soluble in alcohol. At 100°, the salt loses water very slowly and becomes anhydrous—*pyroselenite*—without fusing; at a higher temp. it loses selenium dioxide and forms the normal salt. E. Cornec measured the lowering of the f.p. of mixtures of $2N$-H_2SeO_3, and 0·5N-KOH, in various proportions, and obtained the results illustrated by Fig. 50. A point of inflexion corresponds with the formation of the hydroselenite, and a

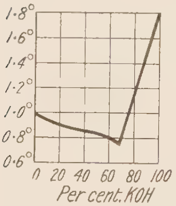


FIG. 50.—Effect of N-KOH on the Lowering of the Freezing Point of $2N$-H_2SeO_3.

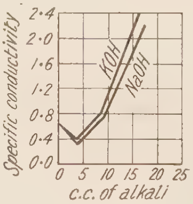
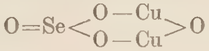


FIG. 51.—Effect of the Progressive Addition of Solution of Alkali on the Specific Conductivity.

minimum in the curve corresponding with the normal selenite. P. Pringsheim and M. Yost studied the Raman effect with aq. soln. of the hydroselenite. A. Miolati and E. Mascetti measured the specific conductivity of a soln. of selenious acid (5 c.c. of which was neutralized with 0·02N-alkali) after the progressive addition of a c.c. of the alkali. The curves shown in Fig. 51 have breaks corresponding with the formation of trihydrodiselenites and hydroselenites. J. J. Berzelius, and L. F. Nilson prepared **potassium trihydrodiselenite,** $KH_3(SeO_3)_2$, as in the case of the sodium salt. The glass-like prisms are probably rhombic, and are permanent in air. The salt is very soluble in water, and it loses about two-thirds of its total water at 100°, and on this account, W. Muthmann and J. Schäfer suggested that it is really **potassium pyroselenite,** $KO.SeO.O.SeO.OH.H_2O$.

L. F. Nilson obtained **rubidium selenite,** $Rb_2SeO_3.H_2O$, and **cæsium selenite,** $Cs_2SeO_3.3H_2O$, by crystallization from the aq. soln. prepared as in the case of the potassium salt. The crystals are obtained with difficulty, and are extremely deliquescent. He also prepared **rubidium hydroselenite,** $RbHSeO_3$, and **cæsium hydroselenite,** $CsHSeO_3$, as in the case of the sodium salt; and likewise also with **rubidium trihydrodiselenite,** $RbH_3(SeO_3)_2$; and **cæsium trihydrodiselenite,** $CsH_3(SeO_3)_2$.

J. J. Berzelius[2] reported a white, insoluble **cuprous selenite** to be formed by digesting cuprous oxide with a soln. of selenious acid; and a pistachio-green, insoluble, basic cupric selenite, by precipitation from a soln. of copper sulphate on adding a soln. of ammonium selenite containing an excess of ammonia. B. Boutzoureano obtained the basic salt, **copper oxyselenite,** $2CuO.SeO_2$, or $CuO.CuSeO_3$,



$$O{=}Se{<}\begin{matrix}O-Cu\\O-Cu\end{matrix}{>}O$$

by heating water and the precipitate obtained by J. J. Berzelius in a sealed tube at 220°; and also by heating the normal salt with a little cupric carbonate and water under similar conditions. The yellowish-green, or dark olive-green, prismatic crystals are monoclinic. They lose selenium dioxide when calcined, leaving a residue of cuprous and cupric oxide. The oxyselenite is insoluble in water, and soluble in aq. ammonia, and in acids. J. J. Berzelius obtained a bulky, curdy, yellowish precipitate on adding ammonium hydroselenite to a warm, aq. soln. of copper sulphite. The precipitate soon forms greenish-blue crystals of **copper selenite,** $CuSeO_3.\frac{1}{3}H_2O$, that is, $HO.Cu.O.SeO.O.Cu.O.SeO.O.Cu.O.SeO.OH$. J. S. Muspratt obtained the same *tetritahydrate* in a similar manner; and B. Boutzoureano, by heating the dihydrate and water in a sealed tube at 150°; or by heating the tetrahydrated hydroselenite at 100°. R. L. Espil obtained the salt, in green rods, by passing the vapour of selenium dioxide over copper oxide, or by heating the mixed oxides in a sealed tube. B. Boutzoureano observed that the greenish-blue crystals he prepared are probably monoclinic. When heated they lose water, and become liver-brown, they then fuse, turn black, and give off their water with ebullition. The salt is insoluble in water, or in selenious acid; but is soluble in acids. L. F. Nilson obtained the dihydrate, $CuSeO_3.2H_2O$, by adding potassium hydroselenite to a soln. of copper sulphate, and allowing the greenish-yellow, amorphous precipitate to stand in the mother-liquor for some time, when it is converted into four-sided, prismatic crystals. C. Friedel and E. Sarasin obtained the same hydrate, as a blue, crystalline powder, in a similar manner by using normal potassium selenite, and also by heating the precipitate with water in a sealed tube at 130°–200°. C. Friedel and E. Sarasin, and B. Boutzoureano, obtained rhombic crystals by allowing a cracked test-tube containing potassium selenite to stand in a soln. of copper sulphate. A. des Cloizeaux and A. Damour found that this salt occurs in thin crusts of transparent, bright blue crystals lining the cracks in the cupriferous lead selenide deposits at Cerro de Cacheuta, Argentine. The mineral was named **chalcomenite**—χαλκός, copper; and μήνη, moon, in allusion to selenium —and it is easily distinguished from the malachite and azurite occurring along with it. A. des Cloizeaux and A. Damour found that the crystals of chalcomenite are monoclinic prisms with the axial ratios $a : b : c = 0{\cdot}72219 : 1 : 0{\cdot}24604$, and $\beta = 89° 9'$; the (001)- and the (101)-faces are often striated; the optical character is negative. The artificial crystals obtained by C. Friedel and E. Sarasin, were found to be rhombic bipyramids with the axial ratios $a : b : c = 0{\cdot}9071 : 1 : 1{\cdot}2322$. The sp. gr. of chalcomenite is 3·76. The salt loses some water at 100°, but when the whole of the water is expelled, some selenium dioxide is simultaneously lost. The salt is permanent in air; and insoluble in selenious acid. C. Freidel and E. Sarasin prepared **copper hydroselenite,** $Cu(HSeO_3)_2$, by heating the normal salt with some water and selenious acid in a sealed tube at 130°–200°; and L. F. Nilson, and B. Boutzoureano, by digesting the normal salt with selenious acid at 60°. The bluish-green powder consists of microscopic prisms. The salt suffers no loss of weight at 100°; it gives off water when heated in a sealed tube; it is insoluble in water, but is decomposed, forming the normal salt. It is soluble in acids. B. Boutzoureano obtained the *monohydrate,* $Cu(HSeO_3)_2.H_2O$, from a soln. of the hydroxide in selenious acid, and by heating the hydroselenite with a conc. soln. of selenious acid in a sealed tube at 230°. The green crystals are monoclinic; they lose 5·1 per cent. of water at 100°. L. F. Nilson reported the *dihydrate,* $Cu(HSeO_3)_2.2H_2O$, to be formed from a soln. of the hydroxide in selenious acid. The blue powder becomes green in warm water. B. Boutzoureano reported the *trihydrate,* $Cu(HSeO_3)_2.3H_2O$, to be formed from a boiling soln. of selenious acid and copper carbonate. The green, rhombic crystals furnish the normal salt at 100°; they effloresce in air; and they are insoluble in water but soluble in acids. L. F. Nilson could not make a more acid copper selenite. W. L. Ray prepared green, crystalline **copper pyroselenite,** $CuSe_2O_5$, by heating selenium oxydichloride, and anhydrous cupric chloride: $CuCl_2+3SeO_2=CuSeO_3.SeO_2+SeOCl_2$. The selenium oxychloride simply acts as a solvent for cupric chloride and selenium dioxide. Selenium dioxide formed by the hydrolysis of some of the selenium oxydichloride by moisture of the air is dissolved in the excess of selenium oxydichloride, and when a certain conc. of selenium dioxide is reached the copper selenite is formed. The reaction may be made to go from right to left by adding selenium oxydichloride that is not sat. with selenium dioxide. Anhydrous cupric chloride and selenium dioxide heated together give selenium oxydichloride and a selenite of copper. F. L. Hahn prepared chromium copper selenite.

J. J. Berzelius[3] obtained **silver selenite,** Ag_2SeO_3, by dissolving silver selenide in boiling nitric acid; the soln. deposits crystals of the salt on cooling. J. Thomsen obtained the salt from a soln. of silver carbonate in selenious acid; and J. J. Berzelius, by adding selenious acid to a soln. of silver nitrate when the selenite is precipitated as a white powder; the salt crystallizes in needles from a soln. in hot, dil. nitric acid, and V. Lenher said, in anhydrous plates; the sp. gr. is 5·9297. J. J. Berzelius said that the salt is not blackened in light; it fuses almost as easily as silver chloride, forming a clear liquid which, on cooling, solidifies to a white, opaque, friable mass having a crystalline fracture. When strongly heated, it gives off selenium dioxide and oxygen, forming silver. It is sparingly soluble in cold water, more freely in hot water; and it readily dissolves in nitric acid, from which soln. it may be precipitated by adding cold water. According to E. Divers and T. Shimidzu, silver selenite is a little more soluble in nitric acid than is silver sulphite; and it is not soluble in a soln. of potassium selenite. J. Thomsen said that when the salt is shaken with bromine water it furnishes selenic acid and silver bromide; and J. Krutwig found that when it is heated in chlorine, silver chloride is formed and selenium dioxide sublimed. B. Boutzoureano evaporated, in air or in vacuo, a soln. of silver selenite in aq. ammonia, and obtained yellow crystals of **silver amminoselenite,** $Ag_2SeO_3.NH_3$. The salt blackens in light; it is insoluble in water and is not decomposed by boiling water; and it is soluble in nitric acid especially if warm. G. Bruni and G. Levi also prepared **silver tetramminoselenite,** $Ag_2SeO_3.4NH_3$. No *gold selenite* has been reported.

According to J. J. Berzelius,[4] **calcium selenite** is gradually deposited during the dissolution of calcium carbonate in a soln. of selenious acid; and L. F. Nilson obtained the *tritatetrahydrate*, $3CaSeO_3.4H_2O$, as a white precipitate consisting of microscopic prisms, when a soln. of calcium chloride is treated with one of sodium selenite. The salt was also prepared by J. S. Muspratt. J. J. Berzelius said that the salt fuses at a red-heat, and in this state has a powerful action on glass, blistering it in a remarkable manner. It is slightly soluble in water. L. F. Nilson found that it effloresces over conc. sulphuric acid losing a mol. of water. J. J. Berzelius, and L. F. Nilson obtained **strontium selenite,** $SrSeO_3.3H_2O$, in an analogous manner; and J. J. Berzelius, J. S. Muspratt, and L. F. Nilson, microscopic prisms of **barium selenite,** which L. F. Nilson regarded as the *monohydrate*, $BaSeO_3.H_2O$. J. B. Krak treated a soln. of selenious acid with baryta-water, and washed the precipitated selenite. O. Pettersson found that barium selenite can be heated to whiteness without decomposition, and at the same temp. the selenate is converted to selenite. J. J. Berzelius obtained small prismatic crystals of **calcium hydroselenite,** from a soln. of the normal salt in selenious acid; and L. F. Nilson obtained monoclinic prisms of the *monohydrate*, $Ca(HSeO_3)_2.H_2O$, when a soln. of a mol of calcium oxide in two mols of selenious acid is allowed to stand over conc. sulphuric acid. The salt is permanent in air; it loses half its selenious acid when heated, or in contact with ammonia; and it is fairly soluble in water. J. J. Berzelius, and L. F. Nilson also prepared **strontium hydroselenite,** $Sr(HSeO_3)_2$; and J. J. Berzelius, J. S. Muspratt, and L. F. Nilson, **barium hydroselenite,** which L. F. Nilson found to be anhydrous, and it is therefore **barium pyroselenite,** $BaSe_2O_5$. L. F. Nilson evaporated at 60° a soln. of the normal salt mixed with an equimolar part of selenious acid, and obtained six-sided plates of **calcium tetraselenite,** $Ca_2Se_4O_{10}.H_2O$, or $Ca_2H_2Se_4O_{11}$, which are stable in air, and freely soluble in water. He could not prepare a barium selenite more acid than the pyroselenite.

J. J. Berzelius mentioned that selenite of beryllium is a white powder; that the hydroselenite is soluble and, when evaporated, dries to a gummy mass; and that both salts lose acid when heated: J. S. Muspratt added that beryllium selenite is in every way analogous to that of aluminium; while the hydroselenite is extremely soluble and does not crystallize. A. Atterberg did not obtain normal beryllium selenite, $BeSeO_3$, but stated that it does not seem to be crystallizable, and its soln. is decomposed by water depositing basic salts. He reported three basic selenites, or **beryllium oxyselenites;** one with the ratios $BeO : SeO_2 : H_2O = 3 : 2 : 6$, was obtained by adding ammonia to a soln. of beryllia, but keeping the soln. acidic, the amorphous precipitate loses about half its water at 100°—a second salt, with the ratios 2 : 1 : 4, was made by adding a soln. of beryllia in selenious acid and treated with ammonia so long as the precipitate formed is redissolved, to a soln. of beryllium oxysulphate, $BeO.BeSO_4$. The amorphous precipitate loses about half its water at 100°. The third basic selenite, with the ratios 7 : 3 : 14, was obtained by adding sodium acetate to the mother-liquor remaining after the separation of the preceding salts. L. F. Nilson obtained a basic salt with the ratios 5 : 2 : 10; this is very near to A. Atterberg's third salt. L. F. Nilson obtained the 5 : 2 : 10-salt by adding normal sodium selenite to a very dil. soln. of normal beryllium sulphate until the precipitate does not dissolve when the soln. is stirred. If the product is treated at 60° with 63·08 per cent. of its weight of selenious acid and a little water, evaporated nearly to dryness, and stirred with a little water, there is formed normal **beryllium selenite,** $BeSeO_3.2H_2O$, in globular masses of a gummy nature, tough and flexible when warm, brittle when cold. If a large excess of water is used, the precipitate is a white, flaky, amorphous, basic salt. L. F. Nilson also reported a number of acidic salts including **beryllium hydroselenite,** $Be(HSeO_3)_2$, obtained in oblique, four-sided plates, by allowing a syrupy soln. of 100 parts of the 5 : 2 : 10-salt in 168 parts of selenious acid to evaporate spontaneously at ordinary temp. He also found that if this soln. is allowed to evaporate at 60°, crystals of the 3 : 5 : 3-salt —**beryllium pentaselenite** — are formed; and the evaporation of the mother-liquor furnishes the

3 : 7 : 5-salt, while a soln. of 100 parts of the 5 : 2 : 10-salt—**beryllium heptaselenite**—and 378·5 parts of selenium dioxide at 60° furnishes the 1 : 3 : 2-salt—**beryllium triselenite.** All these products are said to give microscopic needles ; to be sparingly soluble in cold and hot water ; and to be soluble in dil. hydrochloric acid. There is an indefiniteness about compounds whose claims for recognition as chemical individuals are based on analysis—particularly of gummy, amorphous masses. The subject—*vide* the basic beryllium sulphates, **4.** 28, 11—wants revision in the light of the phase rule.

J. J. Berzelius prepared **magnesium selenite,** as a white, granular mass, by digesting magnesium carbonate with a soln. of selenious acid, and in small, hydrated, four-sided prisms and plates, by evaporating the hot, aq. soln. According to J. S. Muspratt, the rhombic prismatic crystals are those of the *trihydrate,* $MgSeO_3.3H_2O$, isomorphous with magnesium sulphate and carbonate. When heated, the salt loses water and assumes the appearance of an enamel which attacks glass like calcium selenite. According to L. F. Nilson, J. S. Muspratt's trihydrate was deposited from boiling water, and there is some uncertainty if J. S. Muspratt did not mistake the trihydrate for the *hexahydrate,* $MgSeO_3.6H_2O$, which L. F. Nilson prepared by adding sodium selenite to a soln. of magnesium chloride. B. Boutzoureano also obtained it by treating a soln. of magnesium chloride or sulphate with selenious acid, and adding enough sodium carbonate to start the precipitation, which completes itself when the mixture is allowed to stand for some time. L. F. Nilson said that the hexahydrate forms six-sided, rhombic plates ; B. Boutzoureano, tetrahedral crystals belonging to the cubic system. The salt is insoluble in water, but soluble in dil. acids—also selenious acid, especially when warm. When boiled with water, it begins to form a lower hydrate, and when heated in a sealed tube to 150°, it forms monoclinic prisms of the *dihydrate,* $MgSeO_3.2H_2O$. When the hexahydrate is heated to 100°, it loses 5 mols of water, leaving the *monohydrate,* $MgSeO_3.H_2O$, which B. Boutzoureano represented $HO.Mg.HSeO_3$; the dihydrate at 100° also forms the monohydrate. A. Hilger and E. von Gerichten thought that a *heptahydrate,* $MgSeO_3.7H_2O$, is formed as a crystalline precipitate, similar to ammonium magnesium phosphate, when a mixture of magnesium and ammonium chlorides and ammonia—magnesia mixture—is added to a soln. of selenious acid or alkali selenite, and the mixture allowed to stand for some time. When calcined it loses a little selenium oxide ; it is sparingly soluble in water, and freely soluble in acetic and mineral acids. According to B. Boutzoureano, if a soln. of the normal selenite in selenious acid be heated in a sealed tube at 200°, rhombohedral crystals of **magnesium hydroselenite,** $Mg(HSeO_3)_2$, are formed. The salt leaves a residue of magnesia when calcined ; it is insoluble in water, and soluble in acids. L. F. Nilson prepared the *tetrahydrate,* $Mg(HSeO_3)_2.4H_2O$, from a soln. of equimolar parts of the normal selenite and selenious acid. The six-sided prisms are said to be stable in air, and to lose 3 mols. of water at 100°. The salt is freely soluble in water. L. F. Nilson prepared **magnesium tetrahydrotriselenite,** $MgH_4(SeO_3)_3$, by evaporating a soln. of a mol of the normal salt and 3 mols of selenious acid at 60° ; if the evaporation be conducted at ordinary temp., rhombic prisms of the *trihydrate,* $MgH(SeO_3)_3.3H_2O$, are formed.

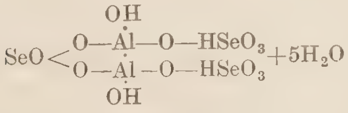
B. Boutzoureano obtained normal **zinc selenite,** $ZnSeO_3$, by heating the hydrate to 200° ; the hydrated salt crystallizes from the mother-liquor obtained in preparing the hydroselenite. The prismatic crystals are probably rhombic. The salt is decomposed by calcination in air, leaving zinc oxide as a residue. It is insoluble in water ; and soluble in acids. L. F. Nilson also obtained this salt by heating the monohydrate with a 52·86 per cent. soln. of selenious acid. L. F. Nilson prepared the *monohydrate,* $ZnSeO_3.H_2O$, as a white, flaky, amorphous precipitate by mixing soln. of zinc sulphate and potassium selenite. If heated with a little selenious acid, it is converted into a microcrystalline powder, which is permanent in air, and when heated to 100°, J. J. Berzelius, and J. S. Muspratt obtained the *dihydrate,* $ZnSeO_3.2H_2O$, as a white precipitate insoluble in water. According to L. F. Nilson, it forms white, four-sided, rhombic prisms when it is allowed to stand in contact with selenious acid. As indicated above, it passes into the anhydrous salt at 200°. J. J. Berzelius said that when the salt is heated, it fuses to a yellow transparent liquid which on cooling forms a white mass with a crystalline fracture; at a higher temp., it gives off selenium dioxide, leaving a basic salt no longer decomposable by heat. When a soln. of zinc selenite in ammonia is evaporated spontaneously in air, in vacuo, or on a water-bath, B. Boutzoureano obtained rhombic crystals of **zinc amminoselenite,** $ZnSeO_3.NH_3$. It is not altered by cold or boiling water; and it does not lose weight at 100°. When heated in a closed tube it gives off water and selenium. J. J. Berzelius said that a soln. of zinc selenite in selenious acid yields a transparent, gummy mass easily soluble in water. L. F. Nilson failed to prepare zinc hydroselenite because of " the great insolubility of the neutral salt " which passes into soln. as tetraselenite. B. Boutzoureano was more successful, since he obtained **zinc hydroselenite,** $Zn(HSeO_3)_2.2H_2O$, by adding powdered zinc carbonate, in small portions at a time, to soln. of 20 grms. of selenium dioxide in 30 c.c. of water; and leaving the clear, decanted, syrupy liquid to stand for some time at 20° to 30°. The colourless, lustrous, monoclinic prisms lose 2 mols. of water at 100°. F. Wöhler obtained **zinc tetraselenite,** $ZnSe_4O_9.3H_2O$, by the action of selenious acid on metallic zinc. The liquid is separated from the selenium and zinc selenide formed at the same time, and when spontaneously evaporated furnishes yellow, oblique, rhombic prisms, which are permanent in air, and easily soluble in water. When the aq. soln. is heated it forms the normal selenide. L. F. Nilson made this salt by treating a mol of the normal salt with a soln. of 3 mols of selenium dioxide and water, and allowing the liquid to evaporate spontaneously.

J. S. Muspratt found that selenious acid does not give a precipitate with a zinc salt, but ammonium selenite furnishes a white precipitate resembling precipitated alumina. It assumes an orange tint when exposed to air; it is soluble in selenious acid; and gives a yellowish-red sublimate when heated in a closed tube. L. F. Nilson prepared **cadmium selenite,** $CdSeO_3$, from a soln. of cadmium hydroxide in hot selenious acid; the liquid suddenly deposited acicular crystals with oblique ends. B. Boutzoureano obtained it in rhombic crystals by heating the hydroselenite with water in a sealed tube at 200°. The salt is insoluble in water, soluble in acids. L. F. Nilson said that the *hemitrihydrate*, $2CdSeO_3.3H_2O$, is formed as a white, amorphous, insoluble precipitate when a soln. of cadmium chloride is treated with sodium selenite. B. Boutzoureano evaporated a soln. of the normal selenite in ammonia, and obtained **cadmium amminoselenite,** $CdSeO_3.NH_3$, as a white, crystalline powder consisting of rhombic prisms which are insoluble in water; soluble in dil. acids; decomposed by hot potash-lye; and decomposed when heated in a sealed tube. B. Boutzoureano also obtained **cadmium dihydrotriselenite,** $2CdSeO_3.H_2SeO_3$, or $SeO(O.Cd.HSeO_3)_2$, from a hot soln. of cadmium carbonate in selenious acid. The monoclinic crystals are insoluble in water, and soluble in acids; they lose water in a sealed tube at 200°, and form the normal selenite. L. F. Nilson found that if a soln. of a mol of the dihydrotetraselenite in 2 mols of selenious acid be evaporated to dryness, and the residue washed with water, small four-sided prisms of the *monohydrate*, $2CdSeO_3.H_2SeO_3.H_2O$, are formed. L. F. Nilson reported cadmium dihydrotetraselenite, $3CdSeO_3.H_2SeO_3$, to be formed from a soln. of cadmium selenite in an excess of selenious acid. L. F. Nilson obtained prismatic crystals of **cadmium pyroselenite,** $CdSe_2O_5$, by digesting 100 parts of a soln. of normal selenite with 139·35 parts of selenium dioxide, and evaporating the liquid at 60°; and B. Boutzoureano, by heating in a sealed tube at 230°, cadmium hydroselenite with three times its weight of water. The rhombic prisms are insoluble in water, and soluble in acids.

L. F. Nilson concluded that mercurous oxide has a great tendency to form basic salts with selenious acid; in circumstances where the normal salt would be expected, the basic salt $Hg_2O : SeO_2=3 : 2$ is formed; and when the hydroselenite would be expected, the 4 : 3 salt was produced. It is therefore assumed that the selenious acid dissolves one part of the base leaving a basic salt as a residue, while an acid salt passes into soln. In other words, the mercurous selenites are very liable to hydrolyze. According to J. J. Berzelius, selenious acid or an alkali selenite gives a white precipitate with mercurous nitrate, and L. F. Nilson represented the composition of the precipitate with selenious acid by $7Hg_2O.6SeO_2.6H_2O$, or $Hg_2O.6Hg_2SeO_3.6H_2O$, **mercurous oxyhexaselenite**; that precipitated by a mol of selenious acid per mol of mercurous nitrate by $3Hg_2O.2SeO_2.4H_2O$, or $Hg_2O.2Hg_2SeO_3.4H_2O$—**mercurous oxydiselenite**—this is the *tetrahydrate*, whereas he obtained the *pentahydrate*, $Hg_2O.2Hg_2SeO_3.5H_2O$, with sodium selenite as precipitant; B. Boutzoureano said that if mercurous oxydiselenite and water or selenious acid be heated in a sealed tube, a mixture of yellow prisms of mercuric selenite and acicular crystals of a mercurous salt is formed. L. F. Nilson observed that if a mol of mercurous nitrate be precipitated by 8 mols of selenious acid, the composition is represented by $4Hg_2O.3SeO_2.6H_2O$, or $Hg_2O.3Hg_2SeO_3.6H_2O$—**mercurous oxytriselenite** is produced. J. J. Berzelius said that the white powder fuses into a dark brown liquid which becomes a lemon-yellow solid and nearly transparent when cold. Hydrochloric acid converts it into mercurous chloride, and some of the selenious acid is reduced to selenium. Potash-lye extracts all the selenious acid. It is not soluble in water or in selenious acid. F. Köhler said that normal **mercurous selenite,** Hg_2SeO_3, rarely occurs in nature; and he obtained it by treating mercurous nitrate by sodium selenite. L. F. Nilson could not prepare the normal salt; E. Divers and T. Shimidzu said that mercurous selenite is not decomposed by potassium selenite into mercury and mercuric selenite. Neither L. F. Nilson nor C. A. Cameron and E. W. Davy were able to obtain *mercurous hydroselenite*, $HgHSeO_3$. F. Köhler found that if the normal selenite be heated below its m.p., dark red **mercurous tetraselenite,** $3Hg_2O.4SeO_2$, is formed as a crystalline mass of sp. gr. 7·350 at 13·5°. It is very little changed by boiling nitric acid; and it gives a sublimate of selenium dioxide when heated. L. F. Nilson found that if a mol of mercurous oxyhexaselenite is treated with 22 mols of selenious acid, **mercurous enneaselenite,** $5Hg_2O.9SeO_2.12H_2O$, is produced as a yellow crystalline powder.

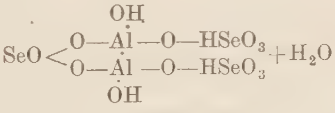
J. J. Berzelius dissolved mercuric oxide in selenious acid and obtained normal **mercuric selenite,** which L. F. Nilson, and B. Boutzoureano represented by $HgSeO_3$. J. J. Berzelius also prepared it by double decomposition. F. Köhler was unable to confirm J. J. Berzelius' observation that the normal selenite is produced by the action of selenious acid on either precipitated or ordinary mercuric oxide at either a high or a low temp. Instead, he obtained a yellow basic salt—**mercuric trioxytetraselenite,** $7HgO.4SeO_2$, or $3HgO.4HgSeO_3$. On the other hand, L. F. Nilson, in agreement with J. J. Berzelius, found that when precipitated mercuric oxide is treated with a soln. of selenious acid no change occurs, but if the liquid be evaporated at 100°, the yellow colour gradually disappears as the acid becomes more conc., and finally a white powder consisting of prismatic crystals is formed. These are washed with water, and dried between bibulous paper. A considerable excess of selenious acid was employed; but the mother-liquor contained no mercuric salt showing that the existence of a soluble hydroselenite is unlikely. B. Boutzoureano prepared normal mercuric selenite in yellow, rhombic plates, by boiling mercurous oxydiselenite with nitric acid. E. Divers and T. Shimidzu found that mercuric selenite is a little more soluble than mercuric sulphite in nitric acid; that mercuric selenite, as well as mercuric oxide, is soluble in a soln. of potassium selenite, and the soln. gives no precipitate with potassium hydroxide. L. F. Nilson found that when a mol of the normal salt is digested with 1 to 3 mols of selenious acid, microscopic needles of **mercuric dihydropentaselenite,** $4HgSeO_3.H_2SeO_3.2H_2O$, are formed. L. F. Nilson could not prepare a more acid salt, but J. J. Berzelius reported **mercuric hydroselenite** to be formed when selenious acid is sat. with mercuric oxide, and the soln. from which the neutral salt has commenced to separate is evaporated. It forms prismatic crystals, longitudinally striated, containing a large proportion of water of crystallization. When heated, the salt fuses in its water of crystallization, it then solidifies, and finally sublimes unchanged in composition. It is freely soluble in water, and slightly soluble in alcohol; the aq. soln. is not precipitated by ammonia; it is slowly precipitated by alkali carbonate; and incompletely precipitated by alkali hydroxide. Sulphur dioxide precipitates mercurous selenite, which soon acquires a pink or scarlet colour owing to the presence of reduced selenium. A. Rosenheim and M. Pritze evaporated a soln. of mercuric chloride with two mols of sodium selenate and obtained white crystals of **sodium mercuric selenite,** $Na_2Hg(SeO_3)_3$, which are fairly stable in air. They are decomposed by water and alkali-lye with the separation of mercuric selenite.

J. J. Berzelius assumed that the precipitate obtained by adding potassium selenite to a neutral soln. of aluminium chloride, or alum, is normal **aluminium selenite,** $Al_2(SeO_3)_3.nH_2O$; J. S. Muspratt analyzed the product, and apparently supported the assumption, for he stated that the white amorphous powder, dried over sulphuric acid, is the *trihydrate,* $Al_2(SeO_3)_3.3H_2O$. Against this, L. F. Nilson showed that a basic salt—**aluminium trioxyenneaselenite,** $4Al_2O_3.9SeO_2.36H_2O$, or $Al_2O_3.3Al_2(SeO_3)_3.36H_2O$—is produced when an excess of aluminium sulphate is treated with sodium selenite. The voluminous, white precipitate loses 16 mols. of water at 100°. The mother-liquor, in spite of the excess of aluminium sulphate, still retains much selenious acid. In order to prepare the normal selenite L. F. Nilson found it necessary to digest the basic salt with the necessary quantity—say 16·2 per cent.—of selenious acid for some time, when the *heptahydrate,* $Al_2(SeO_3)_3.7H_2O$, is obtained as a white crystalline powder. B. Boutzoureano also obtained the salt in a somewhat similar way, and showed that the crystals are hexagonal prisms resembling quartz. L. F. Nilson found that the heptahydrate loses a mol. of water at 100°—B. Boutzoureano said that nearly 5 mols are lost. L. F. Nilson found that the salt is very sparingly soluble in water—B. Boutzoureano said insoluble. The salt is soluble in acids. According to L. F. Nilson, the analysis of J. S. Muspratt in support of the trihydrate is "little worthy of reliance"; but B. Boutzoureano obtained the trihydrate by heating the heptahydrate with 8 to 10 times its weight of selenium dioxide and 15 times its weight of water in a sealed tube at 230°, or by heating the heptahydrate with selenious acid. The octahedral crystals of the trihydrate lose about one-third of their water between 100° and 125°. The trihydrate is said to be insoluble in water, and soluble in acids. B. Boutzoureano obtained rhombic prisms of **aluminium tetraselenite,** $Al_2O_3.4SeO_2.3H_2O$, by heating the heptahydrated normal salt with 8 to 10 times its weight of selenium dioxide and the same weight of water in a sealed tube at 250°. The salt is stable at 100°. He represented the constitution of the normal tri- and hepta-hydrates of the normal selenite, and of the tetraselenite as follows:



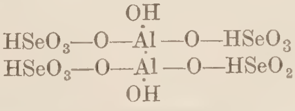
$$\mathrm{SeO}<\begin{array}{l}\mathrm{O{-}\overset{OH}{\dot{A}l}{-}O{-}HSeO_3}\\ \mathrm{O{-}\underset{OH}{\dot{A}l}{-}O{-}HSeO_3}\end{array}+5\mathrm{H_2O}$$

$Al_2(SeO_3)_3.7H_2O$



$$\mathrm{SeO}<\begin{array}{l}\mathrm{O{-}\overset{OH}{\dot{A}l}{-}O{-}HSeO_3}\\ \mathrm{O{-}\underset{OH}{\dot{A}l}{-}O{-}HSeO_3}\end{array}+\mathrm{H_2O}$$

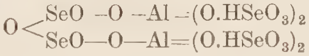
$Al_2(SeO_3)_3.3H_2O$



$$\begin{array}{l}\mathrm{HSeO_3{-}O{-}\overset{OH}{\dot{A}l}{-}O{-}HSeO_3}\\ \mathrm{HSeO_3{-}O{-}\underset{OH}{\dot{A}l}{-}O{-}HSeO_2}\end{array}$$

$Al_2O_3.4SeO_2.3H_2O$

L. F. Nilson reported aluminium hemienneaselenite, $2Al_2O_5.9SeO_2.12H_2O$, to be formed when the basic salt is treated with 81·02 per cent. of its weight of selenious acid—*i.e.* the amount which would be required to form the hydroselenite. No action occurred at ordinary temp., but when warmed, and evaporated, a gummy mass was formed which, on adding cold water, yielded the crystalline salt. J. J. Berzelius said that **aluminium hydroselenite** is formed, as a gummy mass, when the normal salt is dissolved in selenious acid; and L. F. Nilson obtained the *monohydrate,* $Al_2O_3.6SeO_2.5H_2O$, *i.e.* $Al(HSeO_3)_3.H_2O$, from a soln. of the basic salt in 210·64 per cent. of its weight of selenious acid. B. Boutzoureano heated a mixture of one part of the hydrated normal salt, 10 parts of selenium dioxide, and 7 to 8 parts of water at 130°–150°. The white powder consists of monoclinic plates of **aluminium hexaselenite,** $Al_2O_3.6SeO_2.2H_2O$:



$$O\begin{cases}SeO-O-Al=(O.HSeO_3)_2\\SeO-O-Al=(O.HSeO_3)_2\end{cases}$$

L. F. Nilson observed that in its behaviour towards selenious acid, indium resembles aluminium, chromium, cerium, lanthanum, and didymium. He obtained **indium hydroxyselenite,** $In_2(SeO_3)_3.2In(OH)_3.22H_2O$, as an amorphous, slimy precipitate, on adding sodium selenite to a neutral soln. of indium chloride. It loses 19 mols. of water at 100° ; and when digested with selenious acid at 60°, but not completely evaporated, it furnishes acicular prisms of **indium selenite,** $In_2(SeO_3)_3.6H_2O$. It loses 4·6 mols. of water at 100°. If the liquid be evaporated to dryness, and the residue treated with water, acid salts are formed. When a mixture of the basic salt with 65 per cent. of selenious acid is evaporated to dryness at about 60°, and the residue washed with water, **indium hexahydroenneaselenite,** $2In_2(SeO_3)_3.3H_2SeO_3.12H_2O$, or $In_2(SeO_3)_3.2In(HSeO_3)_3.12H_2O$, remains in granular crystals. It loses its water of crystallization at 100°. If the basic salt be digested with 169·91 per cent. of selenious acid ; the soln. evaporated to dryness at 60° ; and the residue extracted with water, there remains a crystalline powder of **indium hydroselenite,** $In_2(SeO_3)_3.3H_2SeO_3.4H_2O$, or $In(HSeO_3)_3.2H_2O$.

L. Marino prepared **thallic selenite,** $Tl_2(SeO_3)_3$, by boiling a freshly prepared soln. of thallic hydroxide with an excess of selenious acid. The white, crystalline mass is insoluble in water, but soluble in dil. nitric acid ; it is decomposed by hydrochloric and sulphuric acids ; and furnishes thallic oxide when treated with alkali-lye. F. Kuhlmann obtained normal **thallous selenite,** Tl_2SeO_3, by oxidizing thallous selenide with nitric acid, or from a sat. soln. of thallous carbonate in selenious acid. The mica-like crystals melt when heated. The salt is freely soluble in water, but insoluble in alcohol and ether. A soln. of the normal salt in selenious acid deposits crystals of **thallous hydroselenite,** $TlHSeO_3$; which are also obtained by adding alcohol to the soln. They are freely soluble in water. F. Franke gave for the electrical conductivity of a soln. of an eq. of the normal salt in v litres of water at 25° :

v . . .	32	64	128	256	512	1024
λ . . .	77·94	89·03	99·55	108·1	116·0	122·7

J. J. Berzelius [5] obtained a white, insoluble powder by double decomposition, and L. F. Nilson showed that the precipitate obtained with a soln. of cerous sulphate and an excess of sodium selenite as a basic salt—**cerous oxypentaselenite,** $Ce_2O(SeO_3)_2.Ce_2(SeO_3)_3.30H_2O$. When a mol of this salt is digested with a warm soln. of a mol of selenious acid, white, insoluble, amorphous **cerous selenite,** $Ce_2(SeO_3)_3.12H_2O$, is formed. S. Jolin also obtained the amorphous salt with 3 mols. of water by adding selenious acid to a soln. of cerous acetate ; it lost half its water at 100°. J. J. Berzelius obtained a soln. of the normal salt in selenious acid and inferred that it contained the acid salt. R. L. Espil prepared anhydrous cerium selenite, as an insoluble, yellow powder, by passing the vapour of selenium dioxide over the heated oxide, or by heating a mixture of the oxides in a sealed tube. L. F. Nilson obtained **cerous dihydrotetraselenite,** $Ce_2(SeO_3)_3.H_2SeO_3.5H_2O$, as a microcrystalline powder, by treating a mol of the basic salt with 7 mols. of selenious acid. S. Jolin obtained a similar product, with 4 mols. of water of crystallization, by treating the normal salt with selenious acid. If the basic salt be treated with 19 mols. of selenious acid, at a moderate heat, L. F. Nilson obtained **cerous hydrosulphite,** $Ce(HSeO_3)_3.H_2O$, in oblique, four-sided, microscopic laminæ. J. J. Berzelius obtained ceric selenite as a lemon-yellow powder by double decomposition ; and

G. A. Barbieri and F. Calzolari, **ceric selenite,** $Ce(SeO_3)_2$, by heating 10 grms. of hexahydrated ceric nitrate, with 12 grms. of selenious acid, and 200 c.c. of nitric acid of sp. gr. 1·40, under a reflux condenser for some hours. The orange-yellow powder is insoluble in water, but slightly soluble in conc. nitric acid. J. J. Berzelius said that a soln. of the yellow salt in selenious acid dries to a soluble, yellow, sticky mass on evaporation.

R. L. Espil prepared colourless, anhydrous **lanthanum selenite,** $La_2(SeO_3)_3$, by passing the vapour of selenium dioxide over the heated oxide, or by heating the mixed oxides in a sealed tube. L. F. Nilson obtained the basic salt—**lanthanum hydroxytetraselenite,** $3La_2O_3.8SeO_2.28H_2O$, or $La_2(SeO_3)_3.La(OH)SeO_3.13H_2O$—as a white, insoluble, amorphous precipitate, by adding an excess of sodium selenite to a soln. of lanthanum sulphate. By using a considerable excess of sodium selenite, he obtained very nearly **lanthanum selenite,** $La_2(SeO_3)_3.13H_2O$. If the basic salt is treated with 40 per cent. of its weight of selenious acid at ordinary temp., there is formed a white, powdery **lanthanum tetrahydropentaselenite,** $La_2(SeO_3)_3.2H_2SeO_3.4H_2O$, consisting of four-sided, oblique tablets. If the normal selenite be dissolved in 120 per cent. of its weight of selenious acid, the soln. evaporated at a gentle heat, and the residue washed with water, there remains **lanthanum hydroselenite,** $La_2(SeO_3)_3.3H_2SeO_3.4H_2O$, or the *dihydrate*, $La(HSeO_3)_3.2H_2O$, as an insoluble powder consisting of four-sided prisms. Again, if lanthanum hydroxide be dissolved in selenious acid, a heavy, white, crystalline powder of the monohydrate, $La(HSeO_3)_3.H_2O$, is formed. P. T. Cleve obtained the same salt by adding alcohol to a mixture of lanthanum chloride and selenious acid. It loses three-fifths of its total water at 100°.

R. L. Espil prepared colourless, anhydrous **praseodymium selenite,** $Pr_2(SeO_3)_3$, by the method used for the cerium salt, and similarly rose-coloured anhydrous **neodymium selenite,** $Nd_2(SeO_3)_3$. L. F. Nilson mixed a soln. of didymium sulphate with an excess of sodium selenite and obtained an amorphous white precipitate with a slight rose tint. Its composition corresponded with **didymium oxyoctoselenite,** $2Di_2(SeO_3)_3.Di_2O(SeO_3)_2.28H_2O$. P. T. Cleve also obtained this salt with 21 mols. of water. L. F. Nilson found that when the basic salt was treated with selenious acid, it furnished a micro-crystalline powder of **didymium dihydrotetraselenite,** $Di_2(SeO_3)_3.H_2SeO_3.8H_2O$, in four-sided prisms. P. T. Cleve obtained this salt, with 4 mols. of water of crystallization, by adding selenious acid and then alcohol to a soln. of didymium nitrate. L. F. Nilson dissolved the basic salt at a gentle heat, with 128·5 per cent. of its weight of selenious acid, and obtained, on evaporation, a lilac-coloured powder of **didymium hexahydroenneaselenite,** $2Di_2(SeO_3)_3.3H_2SeO_3.18H_2O$, containing four-sided prisms. C. von Scheele said that a basic praesodymium selenite is precipitated by sodium selenite from a soln. of praseodymium sulphate; and the basic salt is converted into **praseodymium dihydrotetraselenite,** $Pr_2(SeO_3)_3.H_2SeO_3.3H_2O$, when warmed with selenious acid. R. L. Espil prepared colourless, anhydrous **samarium selenite,** $Sm_2(SeO_3)_3$, by the method used for the cerium salt. P. T. Cleve obtained the basic salt, **samarium oxyoctoselenite,** $2Sm_2(SeO_3)_3.Sm_2O(SeO_3)_2.7H_2O$, as an amorphous precipitate, by adding normal sodium selenite to a soln. of samarium sulphate; if samarium acetate be treated with selenious acid, **samarium dihydrotetraselenite,** $Sm_2(SeO_3)_3.H_2SeO_3.4H_2O$, is formed as a heavy, crystalline powder. C. Benedicks obtained **gadolinium dihydrotetraselenite,** $Gd_2(SeO_3)_3.H_2SeO_3.6H_2O$, as an amorphous precipitate which gradually forms aggregates of small needles. L. F. Nilson added an excess of sodium selenite to a soln. of erbium nitrate, acidified with nitric acid, and obtained a heavy precipitate of **erbium selenite,** $Er_2(SeO_3)_3.5H_2O$. In addition to the *pentahydrate*, L. F. Nilson obtained the *enneahydrate* by using a soln. of the neutral sulphate instead of the acidified nitrate. If a mol of the neutral salt be digested with 3 to 9 mols of selenious acid, at 60°, the soln. evaporated to dryness, and washed with water, there remains a micro-crystalline powder of **erbium dihydrotetraselenite,** $Er_2(SeO_3)_3.H_2SeO_3.3H_2O$, composed of small prisms.

O. M. Höglund and P. T. Cleve also obtained this salt by the action of selenious acid on a soln. of erbium nitrate, with or without the addition of ammonia until a precipitate began to be formed. L. F. Nilson added an excess of sodium selenite to a soln. of yttrium sulphate, and obtained a white, heavy precipitate of **yttrium selenite,** $Y_2(SeO_3)_3.12H_2O$. It is nearly insoluble in water; and it is not affected by dil. selenious acid, cold or hot, but with 42·91 per cent. of its weight of the conc. acid, at 60°, converts it into **yttrium dihydrotetraselenite,** $Y_2(SeO_3)_3.H_2SeO_3.H_2O$, which remains as a micro-crystalline, insoluble powder when the soln. is evaporated to dryness, and washed with water. The same salt was obtained by treating the neutral salt with 128·73 per cent. of its weight of selenious acid, and a more acid salt could not be prepared. P. T. Cleve obtained the dihydrotetraselenite from a soln. of freshly precipitated yttrium hydroxide in selenious acid; and by precipitating a soln. of yttrium nitrate with acid sodium selenite.

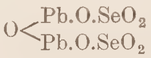
H. Brenek treated α-titanic acid corresponding with 12·64 grms. of TiO_2, with aq. soln. containing respectively 20·39 grms. and 10·43 grms. of selenious acid for a few hours. The precipitates which formed were boiled in their mother-liquid; and after standing a long time in the cold they became crystalline. In the former case **titanyl selenite,** $TiOSeO_3.H_2O$, was formed, and in the latter case the oxyselenite, $2TiO_2.SeO_2.H_2O$, or **titanyl dihydroxyselenite,** $(TiO)_2(HO)_2SeO_3$. The dry salts appear as fine, white powders which are soluble in mineral acids; and are decomposed by alkali-lye. They are more soluble in water than the corresponding selenates. According to J. J. Berzelius, and L. F. Nilson, if a soln. of zirconium oxychloride be treated with sodium selenite, a complex $ZrO_2.3(ZrO)SeO_3.18H_2O$ is formed as a white, slimy, amorphous mass, not at all soluble in water, and dissolving in hydrochloric acid only with difficulty. It loses 15 mols. of water at 180°. O. Kulka made it by the action of zirconium sulphate on a soln. of selenium dioxide in nitric acid. M. Weibull said that the air-dried precipitate has the composition of **zirconyl selenite,** $(ZrO)SeO_3.2H_2O$. L. F. Nilson reported normal **zirconium selenite,** $Zr(SeO_3)_2$, is formed by digesting a mol of the basic salt with 13 mols of selenious acid at 60°. It furnishes microscopic, oblique, four-sided prisms, which at a white-heat yields crystalline zirconia. The *monohydrate,* $Zr(SeO_3)_2.H_2O$, is formed in microscopic, four-sided prisms with oblique ends, when a mol of the basic salt is treated with 5 mols of selenious acid at 60°. It is insoluble in water, and dissolved only with the greatest difficulty in boiling hydrochloric acid. An acid zirconium selenite could not be prepared.

R. L. Espil said that thorium oxide is unchanged when boiled with selenious acid, whereas cerium oxide forms a selenite. P. T. Cleve reported **thorium selenite,** $Th(SeO_3)_2.H_2O$, to be formed as a white, amorphous, insoluble precipitate when thorium chloride is treated with selenious acid, and the washed product dried over sulphuric acid. In addition to this *monohydrate,* L. F. Nilson obtained the *octohydrate,* $Th(SeO_3)_2.8H_2O$, by treating a soln. of thorium sulphate with an excess of sodium selenite. The voluminous, white precipitate shows signs of crystallization. It is insoluble in water, soluble in hydrochloric acid. These acid salts were made by L. F. Nilson: **thorium hexahydroheptaselenite,** $2Th(SeO_3)_2.3H_2SeO_3.13H_2O$, by digesting a mol of the octohydrated selenite with a warm soln. of 2 mols of selenious acid at a gentle heat; **thorium decahydroenneaselenite,** $2Th(SeO_3)_2.5H_2SeO_3.11H_2O$, by evaporating 100 parts of the octohydrated selenite with 35·12 parts of selenious acid; and if three times this proportion of selenious acid is employed, **thorium hexahydropentaselenite,** $Th(SeO_3)_2.3H_2SeO_3.5H_2O$, is formed.

J. J. Berzelius [6] obtained a white powder by treating stannic oxide with selenious acid, and J. S. Muspratt's analysis corresponds with **stannic selenite,** $Sn(SeO_3)_2$. L. F. Nilson obtained it by evaporating a soln. of a mol of the basic salt in 4 mols of selenious acid at about 60°. The crystalline residue is insoluble in water, but it is soluble in an excess of warm hydrochloric acid. If a neutral soln. of stannic chloride be treated with sodium selenite, the voluminous, white precipitate has a composition corresponding with **stannic octohydroxyhexaselenite,** $3Sn(SeO_3)_2.2SnO_2.27H_2O$, or $3Sn(SeO_3)_2.2Sn(OH)_4.23H_2O$; it loses 23 mols. of water at 100°. A soln. of this basic salt in a large excess of selenious acid yields on evaporation a viscid mass so that *stannic hydroselenite* could not be prepared.

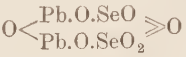
J. J. Berzelius obtained a basic lead selenite by roasting lead selenide; and by calcining normal lead selenite at a high temp.; or by treating it with ammonium carbonate. C. M. Kersten reported normal **lead selenite,** $PbSeO_3$, to occur as a mineral in sulphur-yellow spherical grains or botryoidal masses, with a fibrous fracture either alone or mixed with lead and antimony selenide, malachite, etc., in the Friedrichsglück mine, near Hildburghausen, Thüringerwald. J. D. Dana called the mineral *kerstenite*—*cf.* cobalt arsenide. The data do not distinguish whether the mineral is a selenite or selenate (*q.v.*). E. Bertrand also obtained a white mineral occurring along with chalcomenite and other selenides at Cacheuta, Mendoza, Argentine, which he described as *selenite de plomb*, and named **molybdomenite**—from μόλυβδος, lead, and μήνη, moon. Here again the data are not satisfactory. J. J. Berzelius made the normal selenite, as a white powder, by adding selenious acid or an alkali selenite to a soln. of lead chloride or nitrate. An excess of ammonium selenite added to a soln. of lead chloride gives a good result; with the nitrate the product is contaminated with nitrate. A. Schafarik obtained it as a grey, crystalline mass, by fusing the selenate; and L. Marino obtained it, mixed with a little selenate, by treating lead dioxide with selenious acid. E. Bertrand said that molybdomenite occurs in white, transparent or translucent, lustrous, thin, fragile scales belonging to the rhombic system. The crystals show cleavage in two directions; and they are optically positive. J. J. Berzelius found that the normal selenite melts nearly at the m.p. of lead chloride, forming a yellow liquid which, on cooling, solidifies to a white, opaque mass of crystalline fracture; at a bright red-heat, it gives off selenium dioxide, leaving behind a basic salt. It is very sparingly soluble in water even in the presence of selenious acid; it is decomposed with difficulty by boiling sulphuric acid.

According to L. Marino, when lead dioxide is treated with selenious acid, besides normal lead selenite there is also formed a sulphur-yellow, crystalline powder, with the empirical composition $Pb_2Se_2O_7$, and which he regards as a salt of lead sesquioxide, $Pb_2O_3.2SeO_3$. If lead sesquioxide be regarded as lead plumbate, $Pb[PbO_3]$, lead triselenitoplumbate would be $Pb[Pb(SeO_3)_3]$, and **lead oxydiselenitoplumbate,** $Pb[PbO(SeO_3)_2]$. L. Marino obtained the same product by digesting lead sesquioxide with warm, conc. selenious acid, heating the mixture to its boiling point, filtering, digesting the solid with cold, 7 per cent. nitric acid, and washing. Only a trace of selenate results showing that lead dioxide is not formed as an intermediate product. The yellow, crystalline powder is practically insoluble in water, dil. nitric acid, and dil. sulphuric acid; it is soluble in moderately conc. hydrochloric acid with the evolution of chlorine; it is soluble in alkali-lye; and it liberates iodine from acetic acid soln. of potassium iodide. When this salt is treated with a soln. of potassium carbonate, it yields a mol. each of lead monoxide and dioxide, whilst the addition of dil. nitric acid to a soln. of the salt in 15 per cent. soda-lye precipitates lead sesquioxide: $Pb_2Se_2O_7=Pb_2O_3+2SeO_2$. When the yellow salt is heated to 200°, it gradually changes into a white isomeride which exhibits reactions different from those obtained with the yellow form. For instance, it does not yield lead dioxide when boiled with a soln. of an alkali carbonate. When heated with dil. sulphuric acid and potassium permanganate at 40°-50°, the white salt takes up one atom of oxygen per mol., while the yellow salt is stable, but after a prolonged heating at 80°, it takes up 2 atoms of oxygen per mol. The yellow form is completely decomposed into selenium and lead sulphide by hydrogen sulphide; the white form in acetic acid yields a soln. of selenic acid while part of the selenium is precipitated as such. Oxalic acid quickly oxidizes the yellow form to carbon dioxide, but not so readily as with the white form. It is thence assumed that the two forms are differently constituted, and have the graphic formulæ :



$\mathrm{O}<\begin{matrix}\mathrm{Pb.O.SeO_2}\\ \mathrm{Pb.O.SeO_2}\end{matrix}$

Yellow $Pb_2Se_2O_7$



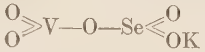
$\mathrm{O}<\begin{matrix}\mathrm{Pb.O.SeO}\\ \mathrm{Pb.O.SeO_2}\end{matrix}\geqslant\mathrm{O}$

White $Pb_2Se_2O_7$

W. Muthmann and A. Clever [7] prepared sodium selenoarsenite, $Na_3AsSe_3.9H_2O$, together with other salts, when arsenic pentaselenide is boiled with a soln. of selenium in sodium hydroxide ; on conc. the filtered soln. in vacuo, a mixture of white needles and orange-red tetrahedra is obtained. On separating these by levigation, a small quantity of the tetrahedra is obtained. It is unstable on exposure to air, becoming coated with grey selenium ; it is easily soluble in water, and the brown soln. when treated with dil. acids gives a brownish-red precipitate with the evolution of hydrogen selenite. According to L. F. Nilson, **antimony oxyselenite,** $Sb_2O_3.2SeO_2.\frac{1}{2}H_2O$, or $(SbO)Sb(SeO_3)_2$, or $Sb_2O(SeO_3)_2.\frac{1}{2}H_2O$, *i.e.* $SeO_3 : Sb.O.Sb : SeO_3$, is produced as a white, crystalline powder consisting of well-developed, oblique, four-sided tablets, by treating precipitated antimony trioxide with conc. selenious acid. It loses its water of crystallization at 100°. By digesting a mol of this salt with 4 to 10 mols of selenious acid, evaporating the soln. at about 60°, and washing the residue with water, there remained a white, crystalline powder consisting of microscopic prisms and plates of **antimony tetraselenite,** $Sb_2O_3.4SeO_2$. I. Pouget prepared **potassium orthoselenoantimonite,** K_3SbSe_3, in the form of orange crystals, by evaporating a soln. of antimony selenide and potassium selenide in a current of hydrogen ; the salt is very unstable, and its soln. rapidly deposits selenium. Similarly with **sodium orthoselenoantimonite,** $Na_3SbSe_3.9H_2O$, which crystallizes in yellow needles from a soln. of antimony selenide and sodium selenide ; it is even more oxidizable than its potassium analogue, and its soln. deposits red, tetrahedric crystals of sodium selenoantimonate, $Na_3SbSe_4+9H_2O$. When a hot, sat. soln. of potassium and antimony selenides is cooled, **potassium selenotetrantimonite,** $K_2Sb_4Se_7.3H_2O$, separates as a gelatinous, brown precipitate ; and similarly with **sodium selenotetrantimonite,** $Na_2Sb_4Se_7$. L. F. Nilson found that when basic bismuth carbonate is boiled with selenious acid, **bismuth selenite,** $Bi_2(SeO_3)_2$, is formed in small, microscopic needles. If bismuth hydroxide be treated with an excess of conc. selenious acid, **bismuth dihydrotetraselenite,** $Bi_2H_2(SeO_3)_4$, is formed in prismatic crystals, generally united in leaf-like aggregates. No higher acid salt could be obtained.

W. Prandtl and F. Lustig [8] found that when vanadium pentoxide is boiled with selenious acid in aq. soln., on cooling, **selenitovanadic acid,** $3V_2O_3.4SeO_2.4H_2O$, separates as a yellowish-red, crystalline, doubly refracting powder which consists of small golden leaflets of the *hexahydrate*, $(3V_2O_5.4SeO_2.4H_2O).6H_2O$, if it is deposited from a soln. containing an excess of selenious acid or if evaporated with hydrochloric acid ; the *decahydrate*, $(3V_2O_5.4SeO_2.4H_2O).10H_2O$, if prepared from equal weights of vanadium pentoxide and selenium dioxide ; and the *dihydrate*, $(3V_2O_5.4SeO_2.4H_2O)2H_2O$, if obtained from aq. soln. of an alkali selenite acidified with dil. sulphuric acid. The water of crystallization is lost at 100°. Two series of **selenitovanadates** were obtained : (i) The red salts are produced by boiling equal weights of vanadium pentoxide and selenium dioxide in water, adding enough alkali hydroxide to form a clear, slightly alkaline soln., and acidifying with acetic acid. (ii) The yellow salts are formed in a similar manner but employing one part by weight of vanadium pentoxide and ten parts of selenium dioxide. (iii) Orange-coloured salts were obtained by the action of an excess of selenious acid on the alkali vanadates at a high temp., and subsequent evaporation. The ratio $R_2O : V_2O_5$ in these salts is generally simple. The selenium dioxide *nicht sehr fest gebunden ist*, so that when boiled with water, the alkali salts are resolved into trivanadate and alkali selenite. Hence these products are to be regarded as compounds of the vanadates with variable quantities of selenious acid. W. Prandtl and M. Humbert regarded the selenitovanadates as derivatives of hexavanadic acid, and they can be formulated in terms of the co-ordination theory. The mol. of hexavanadate can unite with up to 12 mols. of selenious acid. The compound $3V_2O_5.4SeO_2.4H_2O$ is represented as **tetraselenitohexavanadic acid,** $H_4V_6O_{17}.4H_2SeO_3$, and it forms a *tetrahydrate*, and an *octohydrate*. These compounds lose respectively 2, 6, and 10 mols. of water at 100°, forming $3V_2O_5.4H_2SeO_3$.

The following salts were obtained by W. Prandtl and co-workers; **potassium selenitometavanadate,** $K_2O.V_2O_5.2SeO_2$, or $KVO_3.SeO_2$,



$$\begin{matrix}O\\O\end{matrix}\!\geqslant V—O—Se\!\leqslant\!\begin{matrix}O\\OK\end{matrix}$$

as a yellow crystalline powder; **ammonium selenitometavanadate,** $(NH_4)_2O.V_2O_5.2SeO_2$, in small, yellow, doubly refracting needles with parallel extinction and the same salt as a *tritahydrate.* W. Prandtl and co-workers found that tetraselenitohexavanadic acid forms salts when a soln. of alkali vanadate is treated with an excess of a 20 to 25 per cent. soln. of selenious acid. In this way are obtained, orange prisms of **sodium decahydrotetraselenitohexavanadate,** $Na_2H_2V_6O_{17}.4H_2SeO_3$; a bulky precipitate of the *hexahydrate;* and dark red prisms of **sodium hexahydrotetraselenitohexavanadate,** $Na_2H_2V_2O_{17}.4SeO_2.2H_2O$; a bulky orange precipitate of **potassium hydrotetraselenitohexavanadate,** $K_3HV_6O_{17}.4SeO_2$, or of *potassium dihydrotetraselenitohexavanadate,* $K_2H_2V_6O_{17}.4SeO_2$; or of *potassium pentahydrotetraselenitohexavanadate,* $K_3HV_6O_{17}.4SeO_2.2H_2O$; or of *potassium hexahydrotetraselenitohexavanadate,* $K_2H_2V_6O_{17}.4SeO_2.2H_2O$; or of *potassium decahydrotetraselenitohexavanadate,* $K_2H_2V_6O_{17}.4H_2SeO_3$. They also obtained a yellow bulky precipitate of **ammonium trihydrotetraselenitohexavanadate,** $(NH_4)_3HV_6O_{17}.4SeO_2.H_2O$; an orange precipitate of **ammonium dihydrotetraselenitohexavanadate,** $(NH_4)_2H_2V_6O_{17}.4SeO_2$; **lithium decahydropentaselenitododecavanadate,** $2Li_4V_6O_{17}.5H_2SeO_3.24H_2O$, or $2\{2Li_2O.3V_2O_5\}.5SeO_2.29H_2O$, is a red salt very soluble in water and it loses $22H_2O$ in vacuo over sulphuric acid, and $26H_2O$ at 100°; **sodium decahydropentaselenitododecavanadate,** $2Na_4V_6O_{17}.5H_2SeO_3.20H_2O$, or $2\{2Na_2O.3V_2O_5\}.5SeO_2.25H_2O$; **potassium decahydropentaselenitododecavanadate,** $2K_4V_6O_{17}.5H_2SeO_3.8H_2O$, or $2\{2K_2O.3V_2O_5\}.5SeO_2.13H_2O$, forms spherical aggregates of red crystals, or, when air-dried, it gives a red powder consisting of doubly refracting needles; **potassium icosihydrodecaselenitohexavanadate,** $K_4V_6O_{17}.10H_2SeO_3.8H_2O$, or else $2\{2K_2O.3V_2O_5\}.21SeO_2.37H_2O$, is an orange-yellow precipitate; **ammonium pentahydrododecaselenitohexavanadate,** $(NH_4)_3HV_6O_{17}.12SeO_2.2H_2O$; **ammonium enneahydrododecaselenitohexavanadate,** $(NH_4)_3HV_6O_{17}.12SeO_2.4H_2O$; and **potassium enneahydrododecaselenitohexavanadate,** $K_3HV_6O_{17}.12SeO_2.4H_2O$, or $2\{2K_2O.3V_2O_3\}.24SeO_2.8H_2O$, or $2K_2O.3V_2O_3.12SeO_2.4H_2O$, is also orange-yellow; **ammonium decahydropentaselenitododecavanadate,** $2(NH_4)_4V_6O_{17}.5H_2SeO_3.8H_2O$, or $2\{2(NH_4)_2O.3V_2O_5\}.5SeO_2.13H_2O$, crystallizes in large, glistening, dark red, almost opaque, doubly refracting cubes, which are slightly soluble in water, and are decomposed by boiling water; **ammonium silver decahydropentaselenitododecavanadate,** $(2NH_4Ag.NH_3O_3)_4V_6O_{17}.5H_2SeO_3$, or with 8, 12, or $18H_2O$, or $2\{2(NH_4,Ag)_2O.3V_2O_5\}.5SeO_2$, with $12H_2O$, $16H_2O$, or $22H_2O$, is obtained in long, flat, rectangular, glistening, black crystals, by the interaction of silver nitrate and an excess of the red ammonium salt, **potassium hemicosihydrodecaselenitohexavanadate,** $K_3HV_6O_{17}.10H_2SeO_3.14H_2O$, or $3K_2O.5V_2O_5.16SeO_2.40H_2O$, as an orange powder; **potassium heptadecahydroctoselenitohexavanadate,** $K_3HV_6O_{17}.8H_2SeO_3.4H_2O$, or $5\{K_2O.2V_2O_5\}.26SeO_2.43H_2O$, as an orange-yellow crystalline precipitate; **sodium decaselenitotetradecavanadate,** $2Na_2O.7V_2O_5.10SeO_2.13H_2O$, as an orange-yellow flocculent precipitate; **sodium dodecahydropentaselenitohexavanadate,** $Na_2H_2V_6O_{17}.5H_2SeO_3$, with 12 and $32H_2O$, or $2Na_2O.7V_2O_5.12SeO_2$, with $45H_2O$ and $95H_2O$, as orange-coloured separation. A. Rosenheim and L. Krause showed that in preparing *tetraselenitovanadic acid* as the conc. of selenious in the mother-liquor increased from zero to $5N\text{-}H_2SeO_3$, the ratio $SeO_2 : V_2O_5$ in the solid phase increased from 4 : 3 to 5·5 : 3; and likewise also with the ammonium dodecaselenitovanadate. It is therefore concluded that the variable composition of the selenitovanadic compounds is due to the formation of adsorption compounds.

L. F. Nilson [9] added normal sodium selenite to an aq. soln. of chrome alum and obtained a green, amorphous, voluminous precipitate of $4Cr_2O_3.9SeO_2.64H_2O$, *i.e.* **chromium trioxyenneaselenite,** $Cr_2O_3.3Cr_2(SeO_3)_3.64H_2O$, which lost 40 mols. of water at 100°. B. Boutzoureano heated the normal selenite with water in a sealed tube but obtained no basic salt; the product was a mixture of oxide and selenite. J. S. Muspratt added a soln. of potassium or ammonium selenite to a boiling soln. of chromic chloride, and obtained a green, amorphous powder of normal **chromium selenite,** $Cr_2(SeO_3)_3$, soluble in selenious acid, and the soln., on evaporation, furnished a sticky mass. C. Taquet also observed that the product is very sparingly soluble in water, but soluble in hot, conc. hydrochloric acid. It is decomposed at a red-heat into chromic oxide and selenium dioxide. L. F. Nilson said that if a mol of the normal selenite is treated with 3 mols of selenious acid, at ordinary temp., it forms microscopic crystals of the *pentadecahydrate,* $Cr_2(SeO_3)_3.15H_2O$; and B. Boutzoureano obtained rhombic crystals of the *trihydrate,* $Cr_2(SeO_3)_3.3H_2O$, by heating the normal salt with selenious acid. C. Taquet said that if the normal selenite be treated with nitric acid, dark green plates of the *chromium diselenite* are formed—sparingly soluble in water, easily soluble in acids, and decomposed by heat into selenium dioxide and the normal selenite; but B. Boutzoureano could not obtain the diselenite. L. F. Nilson reported **chromium dihydrotetraselenite,** $Cr_2O_3.4SeO_2.13H_2O$, or $Cr_2(SeO_3)_3.H_2SeO_3.12H_2O$, to be formed as a green, crystalline powder by treating a mol of the normal selenite with 15 mols of selenious acid. The mixture was evaporated to dryness at 60°, and lixiviated with water. If 64 mols of selenious acid be employed, **chromium tetrahydropentaselenite,** $Cr_2O_3.5SeO_2.9H_2O$, or $Cr_2(SeO_3)_3.2H_2SeO_3.7H_2O$, is formed.

E. Péchard [10] found that if barium selenitomolybdate is decomposed with sulphuric acid, a yellow soln. of **selenitomolybdic acid** is formed. It can be evaporated to a syrup, but it does not crystallize. A warm soln. of 4 parts of ordinary ammonium molybdate and one of selenious acid, when cooled, furnishes aggregates of needles of **ammonium triselenitodecamolybdate,** $4(NH_4)_2O.10MoO_3.3SeO_2.4H_2O$. When heated, it gives off water, ammonia, and selenium dioxide. It is more soluble in hot than in cold water; and it is insoluble in alcohol. Hydrochloric acid precipitates an acid salt as a gelatinous precipitate which dissolves with decomposition in an excess of the acid. A soln. of 8 parts of ammonium molybdate to one of selenious acid furnishes **ammonium diselenitodecamolybdate,** $4(NH_4)_2O.10MoO_3.2SeO_2.6H_2O$. E. Péchard also prepared potassium triselenitodecamolybdate, $4K_2O.10MoO_3.3SeO_2.5H_2O$, in colourless hexagonal plates; and **potassium ammonium triselenitodecamolybdate,** $4(NH_4,K)_2O.10MoO_3.3SeO_2.5H_2O$, by adding a soln. of potassium chloride to the ammonium salt, or from a mixed soln. of the component salts. Mixed soln. of acid sodium molybdate and selenious acid furnish efflorescent crystals of **sodium triselenitodecamolybdate,** $4Na_2O.10MoO_3.3SeO_2.15H_2O$. The crystals effloresce in air; they are freely soluble in water, and insoluble in alcohol. If a hot soln. of one of the preceding salts be treated with barium chloride, needles of **barium triselenitodecamolybdate,** $4BaO.10MoO_3.3SeO_2.3H_2O$, separate out on cooling; **mercurous triselenitodecamolybdate** is a yellow, amorphous powder; **lead triselenitodecamolybdate** is white, and insoluble even in hot water; and **silver triselenitodecamolybdate** is a yellow, amorphous powder. O. W. Gibbs reported *potassium hexaselenitoheptadecamolybdate,* $5K_2O.17MoO_3.6SeO_2$, to be formed as colourless crystals when potassium phosphomolybdate is treated with potassium selenite. The salt is easily soluble in hot water.

According to W. Prandtl and W. von Blochin, **ammonium diselenitopenta-**

molybdate, $2(NH_4)_2O.2SeO_2.5MoO_3.3H_2O$, is formed in small rhombic prisms when conc. ammoniacal molybdate soln. and ammonium selenite are acidified, and rapidly crystallized. It is readily soluble in water. While **lithium diselenitopentamolybdate,** and **sodium diselenitopentamolybdate** are too soluble to be isolated, **potassium diselenitopentamolybdate,** $2K_2O.2SeO_2.5MoO_3.nH_2O$, furnishes monoclinic crystals of the *dihydrate* and monoclinic crystals of the *pentahydrate*. H. Obpacher obtained isomorphous mixtures of this salt with the corresponding phosphatomolybdate. According to W. Prandtl and W. von Blochin, **rubidium diselenitopentamolybdate,** $2Rb_2O.2SeO_2.5MoO_3.nH_2O$, appears in monoclinic crystals of the *dihydrate* with two forms, one with the axial ratios $a:b:c:=1{\cdot}9129:1:1{\cdot}1840$, and $\beta=106°\ 47'$, and the other with $a:b:c=0{\cdot}4006:1:0{\cdot}9061$, and $\beta=114°\ 28'$—a *pentahydrate* was also prepared; **barium diselenitopentamolybdate,** $2BaO.2SeO_2.5MoO_3.nH_2O$, was obtained in rhombic bipyramids of the *heptahydrate* with the axial ratios $a:b:c=0{\cdot}8282:1:1{\cdot}2039$, as well as crystals of the decahydrate. Water slowly converts ammonium diselenitopentamolybdate into **ammonium diselenitoctomolybdate,** $3(NH_4)_2O.2SeO_2.8MoO_3.nH_2O$, the action is rapid at a high temp. A *pentahydrate* as well as a *hexahydrate* has been prepared. The potassium salt has not been prepared, but barium chloride precipitates **barium diselenitoctomolybdate,** $3BaO.2SeO_2.8H_2O$. Soln. of ammonium molybdate and a selenite are precipitated hot by conc. nitric acid, and they furnish yellow uncrystallizable precipitates, **ammonium diselenitododecamolybdate,** with the ratios $(NH_4)_2O:SeO_2:MoO_3:H_2O=2{\cdot}5:2:12:12$; $2\frac{1}{2}:2:12:20$; and $2:2:12:8$; and likewise **potassium diselenitododecamolybdate,** $2K_2O.2SeO_2.12MoO_3.12H_2O$. By adding nitric acid gradually to the boiling soln., **ammonium hexaselenitohexamolybdate,** $2(NH_4)_2O.6SeO_2.6MoO_3.9H_2O$, as well as products with the ratios $(NH_4)_2O:SeO_2:MoO_3:H_2O=2:7:6:8$; $2:2:5:3$; and $2:2:12:13$ have been prepared.

A. Rosenheim and L. Krause added that the composition of the selenitomolybdates depends on the ratio of molybdate to selenious acid in the soln. from which they were precipitated. When less than one mol of selenium dioxide was present to one mol of molybdate, the potassium and barium salts corresponded with $2R_2O.2SeO_2.5MoO_3\ xH_2O$, and the ammonium salt with $3(NH_4)_2O.2SeO_2.8MoO_3.6H_2O$. With more than one mol of selenium dioxide per mol of molybdate in soln., salts were obtained in which the proportion of base was variable, but the ratio $SeO_2:MoO_3$ was always very nearly 1 : 1, and by adding 15 mols of selenium dioxide to a sat. soln. of ammonium paramolybdate, **ammonium selenitomolybdate,** $2(NH_4)_2O.5SeO_2.5MoO_3.8H_2O$, was obtained in white microscopic prisms; likewise **potassium selenitomolybdate,** $K_2O.2SeO_2.2MoO_3.3\frac{1}{2}H_2O$, in microscopic prisms; and **barium selenitomolybdate,** $BaO.2SeO_2.2MoO_3.7H_2O$, as a white crystalline precipitate. O. W. Gibbs obtained **ammonium selenito-tungstate,** as a crystalline precipitate, from a mixed soln. of ammonium phosphotungstate and selenious acid.

J. J. Berzelius [11] obtained a lemon-coloured powder by adding a selenite to a soln. of a uranyl salt; B. Boutzoureano used uranyl sulphate and sodium selenite, and L. F. Nilson an excess of sodium selenite and uranyl acetate. M. Lobanoff prepared normal uranium selenite, $U(SeO_3)_2$, by adding selenious acid to an acidic soln. of uranic sulphate. A basic salt was also obtained. According to B. Boutzoureano, when the product is heated with water in a sealed tube at 200°, a mass of radiating prisms of **uranyl selenite,** $(UO_2)SeO_3$, is formed. The salt is insoluble in water, and soluble in acids; it leaves behind the oxide, U_3O_8, when calcined. The precipitate itself appears to be the *dihydrate*, $(UO_2)SeO_3.2H_2O$, which loses its water of crystallization at 100°. According to J. J. Berzelius, if the normal selenite be dissolved in selenious acid, and evaporated, it furnishes a transparent sticky mass which, when further dried, forms a soluble, opaque white, crystalline powder which J. S. Muspratt represented by the formula $U_2O_3.3SeO_2$. B. Boutzoureano, however, obtained a voluminous, yellow precipitate of **uranyl dihydrotriselenite,** $2UO_3.3SeO_2.7H_2O$, or $2(UO_2)SeO_3.H_2SeO_3.6H_2O$, or $SeO(O.UO_2.O.SeO.OH)_2.6H_2O$, by adding conc. selenious acid to a soln. of uranyl sulphate and pouring in, *par petites portions*, a soln. of sodium carbonate. The precipitate soon passes into a canary-yellow powder consisting of minute, monoclinic crystals. The salt loses water at 100°, and it is insoluble in water and soluble in acids. L. F. Nilson reported that **uranyl tetrahydropentaselenite,** $3UO_3.5SeO_2.7H_2O$, or $3(UO_2)SeO_3.2H_2SeO_3.5H_2O$, is deposited as a yellow, crystalline powder consisting of rhombic tablets with acute summits, often truncated, when uranyl selenite is digested at 60° with 25·66 per cent. of its weight of selenium dioxide and water. The salt is insoluble in water. If 32 per cent. of selenium dioxide is used the *heptahydrate* is formed in place of the *pentahydrate ;* similarly also with 77 per cent. of selenium dioxide ; and, accordingly, L. F. Nilson added that this seems to be the most acid selenite that can be formed by the action of selenious acid on uranyl selenite. On the other hand, R. Sendtner reported **uranyl hydroselenite,** $UO_2(HSeO_3)_2$, to be formed by the action of selenious acid on hydrated uranyl oxide, or more easily by boiling conc. soln. of uranyl chloride and selenious acid. The lemon-yellow powder, consisting of microscopic crystals, is quite insoluble in water and in an excess of selenious acid. R. Sendtner obtained yellow **ammonium uranyl selenite,** $(NH_4)_2UO_2(SeO_3)_2$, by concentrating a soln. of ammonium uranate in warm selenious acid over sulphuric acid ; yellow **potassium uranyl selenite,** $K_2UO_2(SeO_3)_2$, was obtained in a similar way. Both salts are insoluble.

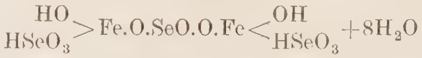
J. J. Berzelius[12] obtained **manganese selenite,** $MnSeO_3.2H_2O$, by adding alkali selenite to a manganese salt ; J. S. Muspratt, by treating manganese carbonate with selenious acid ; and L. F. Nilson, by the action of potassium hydroselenite on a cold soln. of manganese sulphate. The amorphous, colourless precipitate, in contact with its mother-liquor at ordinary temp., gradually forms the crystalline *dihydrate*, and rapidly when heated. The crystals are probably monoclinic. J. J. Berzelius said that the salt readily fuses when heated, and decomposes only in the presence of air, when the manganese is oxidized, and selenium dioxide expelled. The fused salt rapidly attacks glass ; it is insoluble in water. J. S. Muspratt added that it forms a colourless soln. with cold hydrochloric acid, and a pink soln. with the hot acid. L. F. Nilson observed that if normal potassium selenite be employed as precipitant with a neutral soln. of manganese sulphate, the voluminous, white precipitate, in contact with its mother-liquor gradually forms microscopic, four-sided tablets of the *monohydrate*, having a slight yellowish-red tinge. According to J. J. Berzelius, he obtained a crystalline acid salt from a soln. of the normal salt in selenious acid. According to B. Boutzoureano, if the garnet-red soln. of manganese carbonate in very conc. selenious acid at 8° be allowed to evaporate spontaneously at a low temp. in vacuo, amber-yellow crystals of **manganese hydroselenite,** $Mn(HSeO_3)_2.4H_2O$, are formed. The crystals darken on exposure to air, and at 15° they lose water and crumble to a white powder. When treated with hot water, the normal selenite is formed. L. F. Nilson reported that if the normal selenite be heated with 55·5 per cent. of its weight of selenious dioxide, and some water, there is produced a rose-red precipitate of anhydrous **manganese pyroselenite,** $MnSe_2O_5$, consisting of microscopic, oblique, four-sided tablets. The same salt is formed when the neutral selenite is dissolved in 165·5 per cent. of its weight of selenium dioxide and water, and the liquid evaporated. No tetraselenite was formed. B. Boutzoureano obtained the *hemihydrate*, $2Mn.Se_2O_5.H_2O$, or $HSeO_3.Mn.O.SeO{-}O{-}SeO.O.Mn.HSeO_3$, by heating a soln. of manganese carbonate in very conc. selenious acid *en tube scellé* at 200°. The powder, consisting of monoclinic prisms, is not changed by water ; and it is freely soluble in dil. acids.

According to P. Laugier, powdered native manganese dioxide is not readily attacked by a sat. soln. of selenious acid even in sealed tubes, but precipitated hydrated manganese dioxide is readily dissolved with development of heat. The soln. is brown, and seems to contain a selenite of manganese dioxide, but, like the soln. of the dioxide in hydrochloric acid, it readily decomposes, manganese selenate remaining in soln., whilst an orange compound is precipitated. No oxygen is evolved. The precipitate contains manganese sesquioxide and selenium dioxide, but usually retains unaltered manganese dioxide. If a mol of hydrated manganese dioxide be heated with 6 mols of selenium dioxide and water in a sealed tube at 140° for 8–12 hrs., P. Laugier found that **manganic diselenite,** $Mn(SeO_3)_2$, is produced. According to L. Marino and V. Squintani, manganic selenite obtained as just indicated is an orange-yellow, crystalline powder which liberates chlorine from dil. or conc. hydrochloric acid, and iodine from potassium iodide soln. containing acetic acid. With alkali hydroxides or carbonates, manganese dioxide is set free, whilst with oxalic soln., carbon dioxide is liberated quantitatively. It oxidizes mercurous to mercuric salts, cuprous salts to the cupric state, potassium ferrocyanide to ferricyanide, and arsenious to arsenic acid. In presence of a slight excess of alkali hydroxide, it decomposes quantitatively: $MnSe_2O_6{=}MnO_2+2SeO_2$. When heated, the selenite decomposes in the following manner: $MnSe_2O_6{=}SeO_2+MnSeO_4$. At a high temp. and in vacuo, however, the decomposition proceeds according to the equation: $5MnSe_2O_6\rightleftharpoons 8SeO_2+2MnSeO_4+Mn_3O_4+O_2$. Actually, P. Laugier said that **manganic tetraselenite,** $Mn_2Se_4O_{11}$, or $Mn_2O_3.4SeO_2$, is produced by the method first indicated, but L. Marino and V. Squintani observed that manganic selenite is formed and furnishes by decomposition the product observed by P. Laugier. P. Laugier described the tetraselenite as an orange-yellow powder which is insoluble in water, and is not attacked by conc. sulphuric or nitric acid in the cold. If these acids are diluted with three or four times their bulk of water, they have no action on the compound even when boiled. The tetraselenite is dissolved by selenious acid with subsequent precipitation of selenium; it is attacked by cold hydrochloric acid with evolution of chlorine; and it is dissolved by alkali-lye with the formation of a selenite and manganese sesquioxide. It does not lose water at 200°, but at 600° selenium dioxide is volatilized and a rose-coloured residue of manganous selenate is left. If this tetraselenite be heated with water in a sealed tube at 140° for about 4 hrs., small, green prisms of **manganic oxydiselenite,** $Mn_2Se_2O_7$, $Mn_2O(SeO_3)_2$, or $Mn_2O_3.2SeO_2$, are produced. The diselenite does not lose selenium dioxide at 600°, but otherwise it behaves like the tetraselenite. It is also formed by heating a conc. soln. of 2 mols of selenious acid with a mol of hydrated manganese dioxide. B. Boutzoureano also obtained this compound in black crystals by heating a mixture of freshly precipitated, hydrated manganic oxide and an excess of a dil. soln. of selenious acid in a sealed tube at 200°–220°. P. Laugier found that if the diselenite be left in contact with selenious acid for about a month, well-developed crystals of **manganic triselenite,** $Mn_2O_3.3SeO_2.5H_2O$, or $Mn_2(SeO_3)_3.5H_2O$, are formed. These crystals lose water at 200°, and selenium dioxide at 600°.

According to J. J. Berzelius, iron is scarcely attacked by selenious acid, but it becomes covered with a copper-red film of selenium. If a soln. of a ferrous salt be treated with a soluble selenite, a white precipitate, presumably **ferrous selenite** $FeSeO_3.nH_2O$, is formed. When exposed to air, it becomes grey, and then yellow. The fresh precipitate dissolved in hydrochloric acid, forming a soln. which contains some ferric oxide and selenious acid, whilst some selenium is precipitated. Ferrous selenite dissolves in selenious acid, and soon deposits a sparingly soluble acid salt. When the aq. soln. is heated, it gives a brown precipitate containing ferric selenite and selenium. L. F. Nilson did not investigate the ferrous selenites because of the difficulties attending their rapid oxidation.

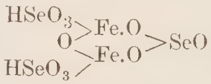
J. J. Berzelius found that **ferric selenite,** $Fe_2O_3.3SeO_2.nH_2O$, or $Fe_2(SeO_3)_3.nH_2O$, is produced by adding an excess of a soluble selenite to a soln. of a ferric salt; J. S. Muspratt added ammonium selenite, and L. F. Nilson, sodium selenite, to a soln. of ferric chloride. The white precipitate becomes dirty-yellow when dried. J. S. Muspratt said that the salt is the *tetrahydrate*, $Fe_2(SeO_3)_3.4H_2O$; L. F. Nilson, the *enneahydrate*, who added that it loses 7 mols. of water at 100°; and B. Boutzoureano, the *decahydrate*, who added that it loses 18·579 per cent. of water at 100°;

23·66, at 110°; 25·69, at 135°; and 26·515, at 150°. On these grounds, B. Boutzoureano represented the formula with 2 mols. of constitutional water:



$$\begin{matrix}HO\\HSeO_3\end{matrix}>Fe.O.SeO.O.Fe<\begin{matrix}OH\\HSeO_3\end{matrix}+8H_2O$$

L. F. Nilson also obtained the *heptahydrate* by acting on the basic salt with enough selenious acid to make the normal salt. B. Boutzoureano prepared the *trihydrate* in apple-green, tetrahedral crystals, by heating equal parts of the decahydrate and selenious acid, and 4 to 5 parts of water in a sealed tube not above 205°; he also obtained greenish-yellow, monoclinic prisms of the *monohydrate*,



by heating the neutral selenite with 2 parts of selenium dioxide and 6 parts of water in a sealed tube at 215°. J. J. Berzelius reported a basic salt, **ferric trioxytriselenite**, $2Fe_2O_3.3SeO_2.nH_2O$, or $Fe_2O_3.Fe_2(SeO_3)_3.nH_2O$, to be formed by digesting the normal or the acid salt in aq. ammonia. It is insoluble in water; L. F. Nilson obtained **ferric oxyoctoselenite**, $3Fe_2O_3.8SeO_2.28H_2O$, or $2Fe_2(SeO_3)_3FeO(SeO_3)_2.28H_2O$, as a voluminous pale-yellow precipitate, by adding selenious acid or an alkali selenite to a soln. of ferric chloride, and he said that it loses 22 mols. of water at 100°. B. Boutzoureano obtained **ferric oxydiselenite**, $Fe_2O(SeO_3)_2$, in rod-like crystals by heating the neutral salt with water in a sealed tube at 230°–250°, for 10 hrs. It is insoluble in water; soluble in acids; and decomposed when heated for a long time with a conc. soln. of sodium carbonate. He also prepared **ferric hydrodiselenite**, $Fe_2O_3.4SeO_2.H_2O$, or $Fe(SeO_3)(HSeO_3)$, by heating one part of the normal selenite, 4 to 6 parts of selenium dioxide, and 12 parts of water in a sealed tube at 250°. The pale-yellow, hexagonal prisms belong to the rhombic system; they are insoluble in water; soluble in acids; and do not lose weight at 100°. L. F. Nilson made the *hemiheptahydrate*, $Fe(SeO_3)(HSeO_3).3\frac{1}{2}H_2O$, in greenish-white, very sparingly soluble crystals, by evaporating a soln. of the basic salt with 59·3 per cent. of its weight of selenium dioxide and water, at a gentle heat; if 16·6 per cent. of selenium dioxide be employed, the *hemienneahydrate*, $Fe(SeO_3)(HSeO_3).4\frac{1}{2}H_2O$, is formed. L. F. Nilson added that he could not make any ferric selenite more acid than these salts. On the other hand, J. J. Berzelius obtained what may be regarded as **ferric hydroselenite**, $Fe(HSeO_3)_3.nH_2O$, by dissolving iron in an excess of a mixture of boiling selenious and nitric acids. As the soln. cools it deposits this salt in pistachio-green laminæ, which give off their water and turn black when heated, and then give off all their selenium dioxide. The salt is insoluble in water but soluble in hydrochloric acid. B. Boutzoureano heated in a sealed tube at 100° a mixture of one part of normal selenite, 8 to 10 parts of selenium dioxide, and 10 parts of water; when all was dissolved, the temp. was raised to 130°–135°, and pale-yellow, monoclinic crystals of **ferric oxytetrahydrohexaselenite**, $Fe_2O_3.6SeO_2.2H_2O$, or $(HSeO_3)_2{=}Fe{-}O.SeO.O.SeO.O{-}Fe{=}(HSeO_3)_2$, were formed.

R. L. Espil obtained anhydrous **cobalt selenite**, $CoSeO_3$, in long, violet prisms, by passing the vapour of selenium dioxide over heated cobalt oxide, or by heating a mixture of the two oxides in a sealed tube. J. J. Berzelius, and L. F. Nilson obtained the *dihydrate*, $CoSeO_3.2H_2O$, as a bluish-red amorphous precipitate on adding sodium selenite to a soln. of cobalt chloride; when heated in the mother-liquor, the precipitate forms a reddish-violet crystalline powder consisting of prismatic crystals. The dihydrate is insoluble in water, but freely soluble in selenious acid. B. Boutzoureano heated a mixture of cobalt carbonate, selenious acid, and water in a sealed tube at 200°, and obtained monoclinic prisms of the *tritahydrate*, $3CoSeO_3.H_2O$, which he represented $HO.Co.O.SeO.O.Co.O.SeO.O.Co.HSeO_3$.

The salt is insoluble in water; soluble in acids; and does not lose water at 100°. J. J. Berzelius said that when the soln. of the normal selenite in selenious acid is evaporated, it furnishes a purple-red, gum-like mass. B. Boutzoureano evaporated in air a soln. of cobalt carbonate in selenious acid and obtained *très beaux cristaux* of **cobalt hydroselenite,** $Co(HSeO_3)_2.2H_2O$. The garnet-red, monoclinic crystals are soluble in water with partial decomposition, forming a violet powder. The water of crystallization is lost at 100°. If a soln. of cobalt carbonate in an excess of selenious acid be heated in a sealed tube at 225°–250°, a violet powder consisting of monoclinic crystals of **cobalt pyroselenite,** $CoSe_2O_5$, is produced. It is insoluble in water, but soluble in dil. acids. L. F. Nilson made it, as a red, glossy mass, by allowing a soln. of the normal selenite in warm conc. selenious acid to evaporate over sulphuric acid; if the conc. soln. be allowed to slowly evaporate at 60° it furnishes what were regarded as rhombic prisms and tablets of the pyroselenite. If a mol of the normal salt and 3 mols of selenious acid be allowed to evaporate slowly at 60°, reddish-violet, microscopic, four-sided tablets of **cobalt triselenite,** $CoSe_3O_7.H_2O$, are formed although complete soln. never occurred. E. Bertrand described minute, rose-red, monoclinic prisms of a mineral which he called **cobaltomenite**—from μήνη, the moon—which he obtained along with molybdomenite from Cacheuta, Mendoza, Argentine. The crystals are optically negative, and were said to contain some cobalt selenite. F. L. Hahn prepared some complex cobaltoselenites; and H. L. Riley obtained **cobaltic pentamminoselenitochloride,** $[Co(SeO_3)(NH_3)_5]Cl$, in brownish-red crystals which in aq. soln. dissociate as a binary electrolyte to the extent of 97 per cent. He also obtained **cobaltic selenitopentamminoselenite,** $[Co(SeO_3)(NH_3)_5]SeO_3.3H_2O$, but it was too deliquescent to purify satisfactorily.

R. L. Espil obtained anhydrous **nickel selenite,** $NiSeO_3$, in yellow crystals by passing the vapour of selenium dioxide over heated nickel oxide, or by heating a mixture of the two oxides in a sealed tube. J. J. Berzelius, and J. S. Muspratt obtained the *hemihydrate*, $NiSeO_3.\frac{1}{2}H_2O$, by treating a soln. of nickel sulphate with potassium selenite; H. Fonzes-Diacon, by oxidizing nickel selenide with nitric acid; and B. Boutzoureano, by heating in a sealed tube at 200° either the precipitated selenite or the product of the action of selenious acid on nickel carbonate along with a very dil. selenious acid. The precipitated selenite furnishes an apple-green powder. The *hemihydrate*, obtained by the sealed tube process, forms stellar groups of green prismatic crystals. B. Boutzoureano represented it by the formula $HSeO_3.Ni.O.Ni.HSeO_3$. L. F. Nilson said that the *dihydrate* is formed in siskin-green, microscopic aggregates of crystals, from a soln. of nickel carbonate in selenious acid at ordinary temp. As observed by J. J. Berzelius, L. F. Nilson found that the evaporation, at ordinary temp., of a soln. of the normal salt in selenious acid furnishes a green, gum-like mass; but if an excess of the normal salt is used, and the soln. slowly evaporated, emerald-green, microscopic, four-sided, quadratic prisms of **nickel hydroselenite,** $Ni(HSeO_3)_2.2H_2O$, are formed. The salt is slowly soluble in water; it is permanent in air; and at 100°, loses its water of crystallization. If a soln. of the normal salt in an excess of selenious acid be slowly evaporated, oblique, four-sided tablets of **nickel tetraselenite,** $NiSe_4O_9.H_2O$, are formed. They dissolve with difficulty in cold water; more readily in hot water. The salt slowly loses water at 100°.

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§ 11. Selenium Trioxide and Selenic Acid

The preparation of **selenium trioxide**, SeO_3, has proved singularly difficult. Many attempts have been made to prepare selenium trioxide analogous with sulphur trioxide, SO_3; whilst the latter is decidedly stable, the former appears to be so unstable as to break down immediately into selenium dioxide and oxygen. E. von Gerichten [1] passed a mixture of the vapour of selenium dioxide and oxygen over red-hot platinum wool, and obtained a white sublimate which he first thought to contain some selenium trioxide, but which he later found to be selenium dioxide alone. C. A. Cameron and J. Macallan also failed to obtain selenium trioxide in this way; nor did they obtain it by heating the selenate of silver, mercury, lead, antimony, bismuth, iron, or platinum. By heating phosphorus pentoxide with selenic acid and cooling the soln., C. A. Cameron and J. Macallan obtained crystals of what they thought to be selenium trioxide. If the temp. is too high the crystals are not produced, and it is thought that the trioxide dissociates at a relatively low temp.—*vide infra*, selenium sulphoxide. R. Metzner could not prepare selenium trioxide by distilling a mixture of selenic acid with phosphorus pentoxide in vacuo. A. Michael and W. T. Conn failed to make the trioxide by digesting anhydrous selenic acid with perchloric acid between 100° and 140° for 4 hrs. The perchloric acid could be distilled from the product unchanged. J. Jannek and J. Meyer unsuccessfully attempted to make the trioxide by the action of dry ozone on selenium, although they found that moist ozone forms selenic acid.

R. R. le Geyt Worsley and H. B. Baker exposed dry selenium dissolved in dry selenyl dichloride to the action of dry ozone and obtained white, solid selenium trioxide mixed with selenyl dichloride. The process can be made continuous by introducing into the oxidation tube sticks of fused selenium. The ozone attacks the dissolved selenium, forming the trioxide, and more selenium dissolves. The selenyl dichloride can be removed by washing, first with thoroughly dried carbon tetrachloride, and then with sodium-dried ether. The ether was finally removed by warm air dried by conc. sulphuric acid and phosphorus pentoxide. The analysis agrees with the formula; and the mol. wt. determined by its effect on the f.p. of phosphoryl chloride agrees with the mol SeO_3. Selenium trioxide is a pale-yellow amorphous solid of sp. gr. 3·6. It decomposes at about 120° without melting or subliming, and it then forms selenium dioxide and oxygen. The sublimate observed in its preparation is said to be due either to the substance having been carried over in fine state, or to an allotropic modification. R. Metzner calculated that the formation of solid selenium trioxide from the dioxide is an endothermal process approximating $(SeO_2,O)=SeO_3-14\cdot7$ Cals.; while its formation from the elements is exothermal, $(Se,3O)=SeO_3+42\cdot1$ Cals. W. G. Mixter gave $(Se,3O)=48\cdot8$ Cals. According to R. R. le Geyt Worsley and H. B. Baker, the trioxide is readily soluble in water with the evolution of heat; it is also soluble in alcohol but insoluble in ether, chloroform, or carbon tetrachloride. It is analogous to sulphur trioxide in forming selenic acid when treated with water, and selenates when treated with alkalies. It reacts with hydrogen dioxide to form a perselenic acid; it is soluble in selenic acid melted under reduced press.; and it furnishes chloroselenic acid when treated with dry hydrogen chloride. J. Meyer and A. Pawletta were unable to confirm the results of R. R. le Geyt Worsley and H. B. Baker; and G. F. Hoffmann and V. Lenher also failed, their product was always selenium dioxide. The existence of the trioxide is therefore "not proven." J. Meyer and A. Pawletta stated that the dissolution of selenium in selenium oxychloride results in the formation of selenous chloride, which is precipitated with selenium dioxide when ozone is passed into the soln. The white sublimate observed by R. R. le Geyt Worsley and H. B. Baker is considered to be selenous chloride. Substitution of glacial acetic acid or carbon tetrachloride for selenium oxychloride does not lead to the separation of selenium trioxide.

In 1827, E. Mitscherlich discovered **selenic acid,** H_2SeO_4. The aq. soln., or combinations as selenates, were made by J. J. Berzelius, and E. Mitscherlich by igniting a mixture of selenium, metal selenides, selenious acid, or the metal selenites along with alkali nitrate; or by passing chlorine through a soln. of potassium selenite mixed with free alkali. H. Rose, and H. Topsöe also obtained the soln. by the action of chlorine on selenium or selenious acid in contact with water; A. J. Balard used hypochlorous acid; J. Thomsen, and H. H. Morris, bromine; R. Metzner, potassium permanganate; F. C. Mathers oxidized a hot nitric acid soln. of selenium dioxide and potassium permanganate—the product is said to be free from selenious acid, but to contain a small proportion of manganese; J. Meyer and K. Heider, sodium dioxide, and hydrogen dioxide; E. Wohlwill, potassium dichromate, lead dioxide, or manganese dioxide; and E. Mailfert, and J. Jannek and J. Meyer, by the action of ozone on selenium in the presence of water. J. Meyer and K. Heider obtained a 47 per cent. conversion by using 30 per cent. hydrogen dioxide on a water-bath; and E. R. Huff and C. R. McCrosky, a 90 per cent. conversion of selenious acid or a selenite, by refluxing with 30 per cent. hydrogen dioxide for 3 hrs. E. Wohlwill found that neither nitric acid nor aqua regia oxidized selenious acid to selenic acid; nitrous acid converts selenium only into selenious acid; whilst mercuric and cupric salts do not oxidize a soln. of selenious acid.

E. Mitscherlich obtained the acid by treating lead selenate suspended in water, with hydrogen sulphide, and concentrating the filtered soln. by evaporation. M. E. Diemer and V. Lenher, and E. von Gerichten employed a modification of this process. E. Wohlwill treated copper selenate with hydrogen sulphide, and evaporated the filtered soln. on a water-bath. E. von Gerichten, and H. Topsöe showed that the precipitated copper sulphide is oxidized during the washing so that the resulting selenic acid is always contaminated with sulphuric acid. This process was employed by J. J. Berzelius, C. Fabian, etc. To get over the objection, C. von Hauer treated calcium selenate with cadmium oxalate, and removed the cadmium from the soln. by precipitation with hydrogen sulphide. The filtered liquid was heated to drive off the excess hydrogen sulphide. J. Thomsen treated a soln. of silver selenite with bromine, and evaporated the filtrate from the silver bromide. G. Metzner found that the product so obtained has a high degree of purity. The filtrate was stated to be free from selenious acid. M. E. Diemer and V. Lenher, V. Lenher and C. H. Kao, P. Klason and H. Mellquist, and E. B. Benger used modifications of this process. L. M. Dennis and J. P. Koller said that the product always contains selenious acid; M. E. Diemer and V. Lenher, and E. B. Benger removed the selenious acid by treatment with hydrogen sulphide, but E. B. Benger observed that some selenic acid is thereby reduced to selenium and sulphur, and probably some sulphur dioxide. M. E. Diemer and V. Lenher stated that the selenic acid obtained by oxidizing silver selenite with bromine is free from selenious and sulphurous acids. R. Metzner prepared selenic acid by first oxidizing selenium dioxide with either chlorine or bromine, neutralizing the acid soln. with copper oxide, separating the copper selenate from the copper chloride by fractional crystallization, and electrolyzing the aq. soln. of copper selenate to remove the copper. He said that the selenic acid so obtained is free from copper, chlorine, and selenious acid. L. M. Dennis and J. P. Koller recommended this process, extracting the copper chloride from the selenate by acetone. They said that this is the best process for preparing selenic acid free from selenious acid and chlorine. J. Meyer and H. Moldenhauer prepared the acid by first oxidizing selenium with nitric acid, and treating the resulting selenious acid with rather more than the theoretical quantity of chloric acid. The soln. was heated to expel chlorine and chlorine oxides, and the soln. heated in vacuo to remove perchloric acid. This gave a soln. with 85–90 per cent. H_2SeO_4; and a yield 90–95 per cent. of the theoretical. P. L. Blumenthal recommended oxidizing selenium dioxide with a mixture of nitric acid and potassium bromate. V. Lenher and E. J. Wechter obtained selenic acid by treating a soln. of potassium selenate with perchloric acid, or a suspension of barium selenate with sulphuric acid.

As indicated above, R. Metzner electrolyzed a soln. of copper selenate to precipitate the copper; and F. C. Mathers electrolyzed lead selenate, resting on the cathode covered with selenic acid, and obtained an 87 per cent. yield of selenic acid. E. Müller effected the electrolytic oxidation of selenites to selenates; when a neutral soln. of sodium selenites is electrolyzed—in a cell using an anode of platinum foil, and a cathode of platinum wire, until all the selenite has disappeared, that is, until a portion of the electrolyte causes no separation of iodine and selenium with a soln.

of potassium iodide. Sodium selenate is obtained by simply evaporating the soln., after filtering it from a small amount of selenium. In the presence of potassium chromate, the deposition of selenium at the cathode is entirely prevented. In order to obtain sodium selenate from the latter soln., the chromium must first of all be removed by precipitation, so that, on the whole, the method of preparing the selenate by electrolyzing the selenite in the absence of potassium chromate is to be preferred. R. T. Glauser prepared selenic acid by the electrolysis of a conc. soln. of selenious acid in conc. nitric acid between 50° and 80° using a small cathode current density, and an anode density of 4 to 5 amp. per sq. cm. for 100 c.c. of soln. A gram of selenious acid was oxidized in 4 to 5 amp. hrs. W. Manchot and A. Wirzmüller obtained selenic acid, free from selenious acid, by the anodic oxidation of selenious acid using a platinum cathode, and an anode of platinum covered with lead dioxide surrounded by a porous pot. The catholyte was $5N$-HNO_3, and the anolyte, conc. selenious acid; and at a low current density and low temp. 1·7 amp. hrs. were required per gram of selenium dioxide (theoretical 0·48). The yield was about 80 per cent. of the theoretical. L. M. Dennis and J. P. Koller found that with the electrolytic process they employed, the electro-oxidation of selenious acid always furnished selenic acid contaminated with selenious acid. C. Manuelli and G. Lazzarini studied the oxidation and reduction that occur in the electrolysis of selenious acid. J. Meyer and K. Heider found the most favourable conditions for the anodic oxidation of selenious acid to be :

> 3·2 grms. of selenium dioxide dissolved in 30 c.c. of nitric acid of sp. gr. 1·4 ; area of platinum foil anode, 6 sq. cms. ; cathode of platinum wire ; temp., 70°–80° ; current, 2·5 to 3·5 amps. at 8 volts. The process was accelerated by the presence of small quantities of selenic acid ; the current efficiency rose from 1 per cent. (after 15 mins.) to 8·3 per cent. (after 111 mins.) and then declined.

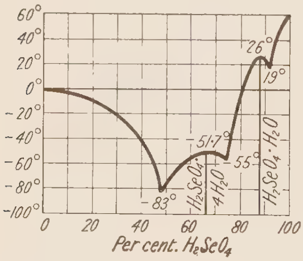

FIG. 52.—Equilibrium Curve between H_2SeO_4 and Water.

C. A. Cameron and J. Macallan cooled by means of liquid sulphur dioxide an aq. soln. of selenic acid, conc. as much as possible—97·75 per cent. H_2SeO_4. The viscid mass was then rubbed with a glass rod, when sudden crystallization accompanied by a rise of temp. occurred. O. Pettersson and G. Ekman concentrated an aq. soln. of selenic acid on a water-bath, and then in vacuo at 180°; on cooling, the solid mass contained 99·9 per cent. of H_2SeO_4. C. A. Cameron and J. Macallan said that if the temp. rises to 217° some selenium dioxide is formed. R. Metzner heated conc. selenic acid in vacuo at 210° for 48 hrs., and cooled the product with methyl chloride when a white, crystalline mass of H_2SeO_4 was obtained. C. A. Cameron and J. Macallan cooled a 88·96 per cent. of selenic acid to —32°, and obtained the *monohydrated* selenic acid, $H_2SeO_4.H_2O$, which was purified by repeated melting and recrystallization. C. A. Cameron and J. Macallan recommended purifying an aq. soln. of selenic acid by converting it into the monohydrate, and repeatedly crystallizing the product, using the seeding process to induce crystallization. R. Metzner also obtained the monohydrate by concentrating an aq. soln. to 210°, and rubbing with a glass rod the viscid mass, cooled to —80°, when crystals are slowly formed. If the viscid mass at 5° or 6° be seeded with crystals of the monohydrate, crystallization readily occurs. The crystals are drained on a porous tile, and dried at a temp. below 15°. C. A. Cameron and J. Macallan also reported that when an 80·11 per cent. soln., corresponding to the dihydrate, is cooled to —51°, a viscid syrup is formed which does not crystallize ; nor does a soln. corresponding with $H_2SeO_4.6H_2O$ crystallize at —40°. R. Kremann and F. Hofmeier determined the f.p. of mixtures of water and selenic acid. The following is a selection from their results :

Per cent. H_2SeO_4	94·9	92·7	91·5	90·7	83·2	79·2	74·7	74·5
Freezing Point	40·2°	26·3°	17·0°	21·9°	13·1°	−7·0°	−53·3°	−55°
Solid phase	H_2SeO_4			$H_2SeO_4.H_2O$				

Per cent. H_2SeO_4	74·5	70·8	57·7	48·0	45·2	38·9	21·0	5·1
Freezing Point	−55°	−55·3°	−61°	−83·0°	−63·5°	−37·2°	−10·5°	−1·3°
Solid phase	$H_2SeO_4.4H_2O$				H_2O			

The results are plotted in Fig. 52. Only two hydrates appear as solid phases: (i) the *monohydrate*, $H_2SeO_4.H_2O$, melting at 26°, and (ii) the *tetrahydrate*, $H_2SeO_4.4H_2O$, melting at −51·7°. The eutectic between H_2SeO_4 and $H_2SeO_4.H_2O$ at 19° corresponds with 91·5 per cent. of selenic acid; that between $H_2SeO_4.H_2O$ and $H_2SeO_4.4H_2O$ at −55° and 74·5 per cent. selenic acid; and that between $H_2SeO_4.4H_2O$ and H_2O at −83° and 48·0 per cent. of selenic acid. D. D. Karve applying the criteria for pseudo-acids found that 98 per cent. selenic acid is a true acid, $H[HSeO_4]$, and in water and alcohol forms a true oxonium salt, $[HSeO_4]H_2OR$, where R represents H or the C_2H_5-radicle. H. Remy discussed the structure of selenic acid.

The conc., aq. soln. of selenic acid is a transparent, colourless liquid. The anhydrous acid, prepared by C. A. Cameron and J. Macallan, and R. Metzner, crystallizes in long, interlacing hexagonal prisms isomorphous with anhydrous sulphuric acid. The molten acid is very prone to undercooling particularly in the presence of impurities—selenious acid. If the selenic acid contains some selenium dioxide, the crystals sometimes appear in the form of double prisms, many of them intersecting in pairs. The slow crystallization of the aq. soln. furnishes large prisms, while rapid evaporation yields needle-like crystals. The monohydrate was obtained in acicular crystals, but with very slow crystallization, rectangular plates were formed. R. Kremann and F. Hofmeier said that the crystallization of the tetrahydrate in undercooled liquids is induced by seeding with the corresponding hydrate of sulphuric acid, thus indicating that these hydrates are isomorphous. The conc., aq. soln. of selenic acid was found by E. Mitscherlich readily to attract moisture from the air, and to develop much heat when mixed with water. Similar results were observed by C. A. Cameron and J. Macallan with H_2SeO_4; and by R. Metzner with the monohydrate.

C. A. Cameron and J. Macallan observed that the **specific gravity** of the molten acid, H_2SeO_4, is 2·6083 at 15°; and when in the solid state, 2·9508 at 15°; similarly with the molten monohydrate, 2·3557 at 15°, and with the solid, 2·6273 at 15°. They gave for the sp. gr. of aq. soln. containing

H_2SeO_4	99·73	97·5	95·0	91·0	87·0	85·0	80·0	73·50 per cent.
Sp. gr.	2·6083	2·5695	2·5163	2·4081	2·3061	2·2558	2·1216	1·9675

The sp. gr. increases with conc. up to the highest conc., and in this respect differs from sulphuric acid. The magnitudes of the increase for similar changes of conc. are not regular, and these differences diminish with increasing conc. of the acid. The presence of selenium dioxide raises the sp. gr., and this is taken to account for the higher values for the sp. gr. obtained by E. Mitscherlich, J. J. Berzelius, and C. Fabian. The following is a selection from the data of M. E. Diemer and V. Lenher for the sp. gr. of aq. soln. containing p per cent. of H_2SeO_4 at 20°/4°:

H_2SeO_4	0·89	5·20	10·05	20·48	40·62	60·73	80·83	99·20 per cent.
Sp. gr.	1·0048	1·0393	1·0768	1·692	1·3895	1·6937	2·1422	2·5925

F. W. O. de Coninck found the sp. gr. of three commercial samples of selenic acid to be 1·4386 at 18°; 1·4669 at 15·5°; and 1·4698 at 15·8°. The **melting point** of the anhydrous acid, H_2SeO_3, found by C. A. Cameron and J. Macallan is 50°; R. Metzner gave 57°. W. Strecker and F. Krafft gave 61°–62° for the m.p. of large crystals. The molten acid shows a marked tendency to undercooling. A similar remark applies to the other hydrates. C. A. Cameron and J. Macallan gave 25° for the m.p. of the monohydrate; R. Metzner, 15°; and R. Kremann and F. Hofmeier, 26°, while the m.p. of the tetrahydrate is −51·7°. R. Metzner gave −3·45 Cals. for the **heat of fusion** of H_2SeO_4, and 4·75 Cals. for the monohydrate. According to R. Metzner, the **vapour pressure,** *p* mm., of anhydrous H_2SeO_4, is:

	100°	105°	140°	190°	210°
p . .	15·8	21·0	28·3	32·0	37·0 mm.

C. A. Cameron and J. Macallan said that the **boiling point** of the monohydrate is 205°. W. Strecker and F. Krafft gave 172° for the b.p. at 85 mm. press.

J. J. Berzelius said that the most conc. acid he could obtain by evaporation contained 4 per cent. of water and had a sp. gr. 2·6; and he added that if the temp. attains 290°, the acid decomposes into selenium dioxide and oxygen. E. Mitscherlich said that if the aq. soln. be evaporated until the temp. has risen to 165°, the sp. gr. is 2·524; if continued to 267°, the sp. gr. is 2·600; if to 285°, 2·625, but part of the selenic acid is then changed to selenious acid. The acid evaporated at 280° contains 84·21 per cent. SeO_2. He added that the tendency to decompose at the high temp. prevents the formation of the pure acid, H_2SeO_4. C. Fabian said that when a selenic acid soln. is evaporated at 265°, the sp. gr. is 2·609, and the liquid contains 94·9 per cent. H_2SeO_4; and if the soln. at 240°–260° be placed over conc. sulphuric acid in a desiccator, which is then evacuated, the liquid has a sp. gr. 2·627, and contains 91·4 per cent. H_2SeO_4. According to C. A. Cameron and J. Macallan, when a dil. aq. soln. of selenic acid is heated in vacuo to 180°, dil. acid distils off until the anhydrous acid remains. The result of further heating is for a time merely to raise the temp.; the acid does not distil in the anhydrous condition. At about 200° it begins to decompose slowly, and at higher temp. rapidly, into selenium dioxide, oxygen, and water. The latter serves to dil. a portion of the remaining acid, which then at once distils. The residue always consisted of a mixture of anhydrous selenic acid with selenium dioxide, the proportion of the latter increasing with the rise of temp. and length of time of heating; the distillate consisted of selenium dioxide mixed with selenic acid. When dil. selenic acid is boiled at ordinary press. nothing but water is evolved until 205° is reached, at which temp. it has the composition of the monohydrated acid. In these respects it behaves like dil. sulphuric acid. After passing 205° the distillate contains at first mere traces of selenic acid, but its conc. gradually increases as the temp. rises from 205° to 260°. At higher temp. a portion of the acid decomposes, the distillate being diluted by the water continuously set free during the decomposition; and at higher temp. much selenium dioxide also distils over. Hence, the conc. of the selenic acid which distils under ordinary press. is always low. If anhydrous selenic acid be strongly heated under ordinary press. a portion of it is decomposed into selenium dioxide, oxygen, and water, the latter serving to dil. the remaining acid. It will then no longer solidify on addition of a crystal of the anhydrous acid. In the case of selenic acid the anhydride is evidently unable to exist free at elevated temp., but breaks up into selenium dioxide and oxygen. When selenic acid is kept for some time at 250° it always contains traces of selenium dioxide, and at 280° decomposition is rapid. Anhydrous selenic acid commences to dissociate in vacuo at about 200°. J. Meyer and H. Moldenhauer observed that when heated above 160°, selenic acid is slowly decomposed into oxygen and selenious acid. According to R. Metzner, the **heat of formation** of the acid, H_2SeO_4, at 15° is $(SeO_2,O,H_2O)=3{\cdot}06$ Cals.; $(Se,2O_2,H_2)=128{\cdot}86$ Cals.; and $(Se,3O,H_2O)=59{\cdot}86$ Cals.; and for the monohydrate with the liquid system $(H_2SeO_4,H_2O)=4{\cdot}80$ Cals.; and with the solid system (H_2SeO_4,H_2O) 4·55 Cals. The **heat of solution** of the solid acid at 15° is $(H_2SeO_4$, 300 c.c. water$)=13{\cdot}35$ Cals., and for the liquid acid, 16·80 Cals.; and the solid monohydrate, 7·45 Cals., and for the liquid monohydrate, −4·75 Cals. J. Thomson gave $(Se,3O,aq.)=76{\cdot}66$ to 77·24 Cals.; $(SeO_2,O,aq.)-19{\cdot}53$ Cals.; and $(SeO_{2aq.},O)=20{\cdot}45$ to 20·50 Cals.; and R. Metzner, $(Se,2O_2,H_2)=145{\cdot}66$ Cals., in soln.; and $(Se,3O,H_2O)-76{\cdot}66$ Cals., in soln. R. Metzner gave for the **heat of neutralization** with 2KOH, 31·31 Cals.; 2NaOH, 31·19 Cals.; BaO, 36·92 Cals.; PbO, 21·64 Cals.; Ag_2O, 22·6 Cals.; and CuO, 18·126 Cals.

J. H. Gladstone and W. Hibbert found that as the conc. of soln. of selenic acid changes with dilution from 41·8 to 27·3 per cent. H_2SeO_4, the **molecular refraction** changes from 29·79 to 29·29 at 24°–25·1°, and the D-line. The calculations are based on the observations of I. Zoppellari on the **index of refraction,** μ. W. J. Pope gave 24·11 for the refraction eq. of the SeO_4-radicle. H. W. Stone found for aq. soln. containing p per cent. H_2SeO_4 at 20° and the D-line—for water alone $\mu=1·3330$:

p . .	1	5	10	20	40	60	80	99
μ . .	1·3341	1·3389	1·3450	1·3583	1·3892	1·4278	1·4810	1·5160

C. Schaefer and M. Schubert observed that the **ultra-red reflection spectra** of the selenates show a definite maximum in the region of 11μ, and this is attributed to the vibrations of the SeO_4-radicle, and it is analogous to the maximum at 9μ exhibited by the sulphates. When the selenates contain water of crystallization, the characteristic water bands appear. The reflection maximum shown by the uniaxial crystals of selenates at about 11μ can be resolved into two groups of characteristic vibrations, and into three in the case of bi-axial crystals. Observations were also made by A. M. Taylor.

G. Gore observed that a **thermoelectric current** is developed with a mercury electrode in contact with an aq. soln. of selenic acid; with dil. soln., the strength of the current is reduced with the increase of conc., but with conc. soln. this phenomenon is reversed. W. Ostwald gave the **electrical conductivity,** μ, of soln. with a mol of the acid in v litres of water at 25°:

v . .	4	16	64	256	1024	4096	8192
μ . .	103·2	107·4	127·3	150·6	169·1	177·1	176·9

A. Miolati and E. Mascetti studied the sp. conductivity of selenic acid to which sodium hydroxide is progressively added. M. S. Sherill and E. F. Izard calculated the reduction potential of the reaction: $H_2SeO_3+H_2O_{\text{liquid}}=3H^{\cdot}+HSeO_4'+2\ominus$ to be $-1·088$ volts; and the free energy of $HSeO_4'$, $-107·71$ cals. at 25°.

J. Thomsen placed selenic acid, 0·45, in his avidity table between sulphuric acid (0·49), and trichloracetic acid (0·36) with hydrochloric acid unity. According to C. A. Cameron and J. Macallan, anhydrous selenic acid possesses a powerful affinity for **water,** absorbing it quickly from the atm. Their combination is attended with contraction and considerable evolution of heat, but less so than in the case of water and sulphuric acid. Like the latter, it disintegrates and blackens many organic substances, such as cork, indiarubber, etc. From others it withdraws the elements of water; thus, alcohol heated with it yields ethylene, and glycerin, acrolein. On cellulose it has an action similar to that of conc. sulphuric acid, paper being converted by it into a tough parchment-like substance. For this reason it should not be filtered through filtering paper, except when cold and very dil. The hot, surfused acid dissolves **iodine,** forming a brown soln. E. Mitscherlich observed that selenic acid decomposes when boiled with **hydrochloric acid,** forming chlorine and selenious acid. O. Pettersson, and F. A. Gooch and P. S. Evans based an analytical process on this reaction. F. A. Gooch and W. H. Scoville found that in the presence of **hydrobromic acid**—potassium bromide in sulphuric acid soln.—selenic acid is reduced to selenious acid. The completeness of the reaction depends on the conc. of the soln., and the proportions of potassium bromide and sulphuric acid which are present. Bromine distils off when the soln. is heated, and if the distillation be continued too long, selenium is liberated, and if the potassium bromide is in too large excess, it is difficult to remove all the bromine before the reduction to selenium occurs. F. A. Gooch and W. G. Reynolds said that **hydriodic acid** slowly reduces selenic acid to selenious acid if a great excess of hydrochloric acid is not present.

C. A. Cameron and J. Macallan observed that when powdered **sulphur** is mixed with liquid anhydrous selenic acid, there is no action in the cold; but if the mixture be heated to 63°, the sulphur dissolves in the acid with the production of an exceedingly deep indigo-blue colour. There is some action, but slight, at 58°. The body which is produced is very unstable, since it begins to decompose at the temp. at which it is formed, with evolution of sulphur dioxide, and reduction of the selenic acid to selenious acid. If water be added when the colour has first developed, sulphur is deposited in soft yellow flakes; but after decomposition has commenced, the addition of water throws down red selenium chiefly, owing to the reaction between the sulphurous and selenious acids which are formed—*cf.* the action of sulphuric acid on sulphur. F. Krafft and O. Steiner found that when anhydrous selenic acid is slowly heated to 55° with sulphur in an atm. of carbon dioxide in a sealed tube, sulphuric acid and selenium are formed. E. B. Benger also observed the sulphur reduces anhydrous selenic acid at 63°; and in aq. soln. at higher temp. Thus, a 94·2 per cent. soln. of the acid is attacked at 68°, and a 40 per cent. soln. at 190°. E. Mitscherlich, B. Brauner, and H. H. Morris said that selenic acid is not reduced by **hydrogen sulphide**, but E. B. Benger found that this statement is not correct because selenic acid of any conc. may be completely decomposed by hydrogen sulphide at any temp. over −10°. The rate of reduction increases both with the temp. and with the conc. of the acid. A 10 per cent. soln. of selenic acid at 45° is completely decomposed by dry hydrogen sulphide in 13½ hrs. The reaction is symbolized: $H_2S+H_2SeO_4=2H_2O+SO_2+Se$; and the sulphur dioxide then reacts with the hydrogen sulphide depositing sulphur. This makes the reaction $3H_2S+H_2SeO_4=4H_2O+Se+3S$. The reaction, however, is still more complex—*vide infra*, sulphur dioxide. L. M. Dennis and J. P. Koller, and A. E. H. Tutton also said that hydrogen sulphide and selenic acid always yield selenium or selenium sulphide; but H. W. Stone found that selenic acid—freed from selenious acid—after dilution to a 5 per cent. or lower conc., can be subjected to a rapid stream of hydrogen sulphide without showing the slightest trace of a yellow coloration. E. Mitscherlich reported that **sulphur dioxide** has no action on selenic acid, but E. B. Benger said that the selenic acid is reduced by a reaction: $H_2SeO_4+3SO_2+2H_2O=3H_2SO_4+Se$, which really takes place in two stages: $H_2SeO_4+SO_2=H_2SO_4+SeO_2$, and $SeO_2+2H_2O+2SO_2=Se+2H_2SO_4$—selenium dioxide has been isolated in the intermediate product. When the sulphuric acid has attained a certain conc., the reducing action ceases, but when the soln. is diluted, the reaction can proceed to completion. According to C. A. Cameron and J. Macallan, solid selenic acid is soluble in conc. as well as in fuming **sulphuric acid**; while **selenium** reacts with anhydrous selenic acid in the cold. The selenium dissolves in the acid with production of an intense green colour. The presence of a minute quantity of water prevents the colour from developing fully until the acid is warmed. The acid is capable of dissolving a considerable quantity of selenium. If kept in a closed vessel the colour thus produced is very permanent, being unaffected for months during summer weather, but if the acid be heated to 75° the colour disappears, and the selenic acid is found to be partly reduced to selenious acid. Addition of water, when the colour has developed, throws down a voluminous red precipitate of selenium, and exposure to the air in an open vessel for a few minutes is sufficient, from the same cause, to change the green colour to the red. E. B. Benger also observed that selenium, at room temp., reduces selenic acid at all conc., and more rapidly at more elevated temp. Conc. soln. are more readily attacked than dil. soln. C. A. Cameron and J. Macallan found that **selenium dioxide** dissolves in hot, anhydrous selenic acid, but the greater part crystallizes out again on cooling. There is no evidence of the formation of an acid analogous to dithionic acid. It was also found that **tellurium**, like selenium, reacts with anhydrous selenic acid in the cold with production of a purple-red colour. Even when the acid is not perfectly anhydrous, it will still give a coloration in the cold. The compound thus formed is probably very unstable, since the colour disappears at so low a temp. as 19°, the selenic acid being partly reduced to selenious acid. If water be added when the colour has developed, tellurium is thrown down in sooty flakes, and exposure to moist air produces the same effect—*vide* tellurium sulphotrioxide.

E. C. Franklin and C. A. Kraus found that selenic acid is insoluble in liquid **ammonia.** P. Jannasch and W. Heimann observed that when selenic acid is boiled with the hydrochloride of **hydroxylamine,** it is quantitatively reduced to selenium; and A. Gutbier noted that selenic acid is slowly reduced by **phenyl hydrazine** with cold, and rapidly in boiling soln. A conc. alcoholic soln. of selenic acid forms an addition compound with phenyl hydrazine. V. Lenher and J. H. Mathews found that **nitrogen peroxide** reacts with conc. selenic acid, cooled with solid carbon dioxide, forming *nitrosylselenic acid*, $(NO)_2SeO_4$—*vide* **8.** 49, 65. L. Rosenstein said that red **phosphorus** reduces the selenates either to the element or phosphide. For the action of **phosphorus pentoxide,** *vide supra*, selenium trioxide. C. A. Cameron and J. Macallan observed that anhydrous selenic acid reacts violently with **phosphorus pentachloride** in the cold; and with **phosphoryl chloride** when warmed slightly—the reaction is attended by the copious evolution of gas, and reduction to lower compound.

M. Dubinin studied the adsorption of selenic acid by **carbon.** According to C. Fabian, conc. selenic acid reacts with **alcohol** with the evolution of heat, forming ethyl selenate, and R. J. Elliot studied the action of the acid on methyl alcohol. C. Chabrié observed that **benzene** reacts with selenic acid, and C. I. Istrati obtained what he believed to be phenyl selenide as a product of the action; H. W. Doughty and F. R. Elder also observed a slow reaction between **toluene** and selenic acid. F. W. O. de Coninck and E. Chauvenet observed that **formic acid** when boiled with selenic acid produces a dark reddish-brown precipitate of selenium; and similar results were obtained with **oxalic, malonic, and pyruvic acids.** The precipitate resembles that produced by the action of sulphur dioxide on selenic acid. Neither **acetic acid** nor **succinic acid** reduces selenic acid. A. B. Lamb found that selenic acid is energetically reduced by **acetyl chloride** at 0°.

E. Mitscherlich found that warm, conc. selenic acid dissolves **copper** and **gold,** but not **platinum,** forming selenious acid; and it dissolves **zinc** and **iron** with the liberation of hydrogen. H. Hradecky found that alloys of gold, and silver, and of palladium dissolve in selenic acid; and that with platinum and silver alloys, the silver passes into soln. leaving the platinum undissolved. H. N. Warren mentioned the possible effect of selenic acid as an impurity in the nitric acid on the parting process in the assay for gold. According to F. Hundeshagen, gold is dissolved by a hydrochloric acid soln. of selenic acid. A. E. H. Tutton found that **iron** in contact with selenic acid becomes covered with a film of selenium which greatly retards the reaction and renders this method practically useless. No hydrogen is evolved, and the formation of the selenium would appear to be due to the reducing action of nascent hydrogen on the selenic acid, $6H+H_2SeO_4=Se+4H_2O$. The net result of such slow action as occurs may therefore be represented by the equation $3Fe+4H_2SeO_4=3FeSeO_4+Se+4H_2O$. When the iron is replaced by zinc, hydrogen is given off, and very little reduction of selenic acid occurs. In the case of **magnesium,** hydrogen is also evolved, but reduction takes place to a considerable extent. C. A. Cameron and E. W. Davy found that when selenic acid is heated with an excess of **mercury,** mercury selenite is formed: $Hg+H_2SeO_4=H_2O+HgSeO_3$; with an excess of selenic acid, the mercury selenite first formed reacts with the acid, forming mercury selenate. K. Hradecky showed that **palladium,** like gold and silver, dissolves completely in selenic acid. Dissolution occurs at ordinary temp. when the metal is in the spongy condition or when it is finely divided if a 67 per cent. acid is used. When the coherent metal in the form of foil or wire is used, soln. only occurs very slowly, even on heating. A deep, reddish-brown soln. is produced, which on concentrating gives a mixture of palladous selenate and selenious acid. K. Hradecky also found that cold selenic acid has no appreciable action on **osmium**; at about 120°, however, the metal is dissolved to form a colourless soln. which contains selenious acid and osmium tetroxide but no selenate. Selenic acid acts as a dibasic acid, forming normal **selenates,** $R_2'SeO_4$, and **hydroselenates,** $R'HSeO_4$; it also forms a number of complex salts; and also mixed salts—selenatosulphates.

The action of bases and salts is therefore discussed in connection with the selenates.

R. R. le Geyt Worsley and H. B. Baker[2] said that both selenium trioxide and chloroselenic acid react with hydrogen dioxide to form **perselenic acid,** since a blue colour is produced with an alcoholic soln. of benzidine. L. M. Dennis and J. P. Koller electrolyzed soln. of potassium selenate, and of selenic acid, under conditions most favourable to the formation, under the analogous cases, of potassium persulphate or persulphuric acid, but in no case was any indication of the formation of a perselenate or perselenic acid observed. E. Mulder inferred that because the electrolysis of a soln. of silver selenate produces no change, and of the fact that selenic acid is an oxidizing agent towards hydrochloric acid, a perselenic acid of the formula H_2SeO_5 cannot exist. L. M. Dennis and O. W. Brown prepared **potassium perselenate,** $K_2Se_2O_8$, by the electrolysis of a sat. soln. of potassium selenate containing a little free selenic acid; platinum electrodes are employed, and the temp. is kept at 4°. The salt has not been obtained free from the selenate, the highest percentage of perselenate in the product being 74·44. Potassium perselenate, when hot, converts manganese dioxide into potassium permanganate, and rapidly oxidizes ferrous and thallous sulphates in the cold. When an aq. soln. of the salt is warmed, oxygen is evolved. They were unable to prepare **thallous perselenate** from potassium perselenate and thallous sulphate because of the oxidation of the thallous sulphate in the cold.

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§ 12. Selenates

Rectangular plates of normal **ammonium selenate,** $(NH_4)_2SeO_4$, were obtained by J. W. Retgers[1] from a soln. of selenic acid neutralized with ammonia or treated with a slight excess of ammonia ; the salt was also made by C. von Hauer, and A. E. H. Tutton. F. C. Mathers and co-workers obtained ammonium selenate by the action of ammonium carbonate on barium or lead selenate. C. von Hauer said that the rhombic crystals are isomorphous with those of ammonium sulphate. H. Topsöe found that the crystals belong to the monoclinic system, and have the axial ratios $a:b:c=1{\cdot}2065:1:1{\cdot}9013$, and $\beta=64°\ 27'$, and he added that the crystals are not related to those of ammonium sulphate ; A. E. H. Tutton gave for the holohedral monoclinic crystals $1{\cdot}8900:1:1{\cdot}1987$, and $\beta=64°\ 31'$. C. F. Rammelsberg suggested that ammonium selenate must be dimorphous, one form being isomorphous with ammonium sulphate, but J. W. Retgers could not support this hypothesis. A. E. H. Tutton tried crystallizing the soln. at various temp., but obtained only the monoclinic form ; and similar results were obtained with soln. of the salt in glacial acetic acid. A. E. H. Tutton showed that the rhombic crystals obtained by C. von Hauer gave a sp. gr. corresponding with the presence of 27 per cent. of rhombic ammonium sulphate, and that the ammonium selenate in the isomorphous mixture takes on the rhombic form. Some acicular crystals in C. von Hauer's preparation are monoclinic. It is hence concluded that ammonium selenate is dimorphous, and the solid soln. which the selenate forms with the sulphate are isodimorphous. The crystals may be prismatic, acicular or tabular, twinning is common on a plane perpendicular to the normal to (001). The (100)-cleavage is perfect ; the (001)- and (010)-cleavages are not as complete. The optical axial angles are :

	Li-line.	*C*-line.	Na-line.	Tl-line.	*F*-line.
$2E$	59° 1′	59° 22′	60° 44′	61° 33′	62° 29
$2V$	37° 10′	37° 19′	37° 54′	38° 22′	38° 44′

J. W. Retgers gave 2·197 for the sp. gr., and O. Pettersson 81·45 for the mol. vol. A. E. H. Tutton gave 2·194 for the sp. gr. at 20°/4°, and 81·12 for the mol. vol. The topic axis $\chi:\psi:\omega=4{\cdot}5939:4\ 2968:5{\cdot}1506$. H. Schröder also made some observations on the mol. vol. A. E. H. Tutton gave for the refractive indices at ordinary temp.—say 10° :

		Li-line.	*C*-line.	Na-line.	Tl-line.	*F*-line.	*G*-line.
10°	α . .	1·5561	1·5571	1·5607	1·5641	1·5687	1·5752
	β . .	1·5584	1·5594	1·5630	1·5665	1·5713	1·5781
	γ . .	1·5796	1·5806	1·5846	1·5885	1·5935	1·6005
80°	α . .	1·5556	1·5563	1·5599	1·5637	1·5682	—
	β . .	1·5560	1·5568	1·5605	1·5643	1·5689	—
	γ . .	1·5764	1·5773	1·5852	1·5852	1·5900	—
100°	α and β	1·5553	1·5561	1·5598	1·5636	1·5682	—
	γ . .	1·5157	1·5765	1·5804	1·5843	1·5890	—

The birefringence $\gamma-\alpha$ is therefore 0·0235 for Li- and *C*-light; 0·0239 for Nalight; 0·0244 for the Tl-light; 0·0248 for *F*-light; and 0·0253 for *G*-light. The sp. refraction for the *C*-ray is $\alpha=0·1468$, $\beta=0·1473$, and $\gamma=0·1519$; and for the *G*-ray, $\alpha=0·1507$, $\beta=0·1514$, and $\gamma=0·1561$. The mol. refractions, respectively, by the μ^2- and the μ-formula, are $\alpha=26·13$ and 45·22; $\beta=26·22$ and 45·41; and $\gamma=27·03$ and 47·13 for the *C*-ray. The indices of refraction for soln. containing 48·20 and 43·88 per cent. of salt in soln., and having the respective sp. gr. 1·3627 and 1·3248 at 20°/4°, are:

Sp. gr.	Li-line.	*C*-line.	Na-line.	Tl-line.	*F*-line.	*G*-line.
1·3627 . .	1·4067	1·4073	1·4098	1·4122	1·4154	1·4198
1·4348 . .	1·4990	1·4996	1·4020	1·4034	1·4073	1·4114

and the mol. refractions of the salt in soln. are 46·84 and 46·74 respectively. C. Schaefer and M. Schubert examined the reflection ultra-red spectrum. A. E. H. Tutton found that water dissolves rather more than its own weight of salt at ordinary temp., and nearly twice its weight is dissolved by boiling water. 100 parts of water dissolve 117 parts of salt at 7°; 164 parts at 59°; and 197 parts at 100°, so that the solubility is slightly greater than that of potassium selenate, and nearly twice as great as that of ammonium sulphate. The super-solubility curve is derived from 142·5 parts of salt in 100 parts of water at 25°; 130·22, at 19·5°; 126·8, at 16·2°; and 124·35, at 1°. The super-solubility curve thus runs nearly parallel with, and very close to, the solubility curve at the lower temp. in the neighbourhood of ordinary temp., and that the two curves diverge from near 20° onwards at an accelerating rate. Hence at the ordinary temp. there is but a very narrow range of metastability between the unsaturated and the labile condition, while the range is considerably greater at a warm summer temp. Alcohol, and acetone do not appreciably dissolve the salt; but it is freely soluble in glacial acetic acid. C. A. Cameron and E. W. Davy found that all the hydrogen atoms can be displaced by bivalent mercury; and when ammonium selenate is heated, it loses ammonia and forms **ammonium hydroselenate,** $NH_4(HSeO_4)$. H. Topsöe prepared the hydroselenate by adding an excess of selenic acid to an aq. soln. of ammonia; and cooling the liquid. The crystals are usually columnar, and rarely tabular. The sp. gr. is 2·162. When heated, the salt decomposes into selenium, selenium dioxide, water and nitrogen.

E. Rimini and G. Malagnini prepared **hydrazine selenate,** $N_2H_4.H_2SeO_4$, by mixing a soln. of a mol of selenic acid (sp. gr. 1·4) dissolved in 2 vols. of alcohol with a mol of hydrazine hydrate (50 per cent.) in 4 vols. of alcohol at 0°. The salt, after filtration, is washed with alcohol, and ether. The salt is not very stable when dry; it burns when heated, and if in large masses it may explode. The salt is freely soluble in water; and the mol. of salt in aq. soln. is $N_2H_4.H_2SeO_4$. The strongly acid aq. soln. soon becomes red owing to the separation of selenium. It forms a complex salt with copper selenate (*q.v.*). J. Meyer and W. Aulich also observed that hydrazine hydrate and dil. selenic acid furnish colourless hydrazine hydroselenate, which is not decomposed by boiling water. When dry, it is caused to explode with unusual readiness by heat, shock, or gentle trituration. It explodes violently on contact with hydrochloric acid vapour so that in analytical practice, selenic acid and selenates should be reduced to selenites by hydrochloric acid before hydrazine hydrate is added.

H. Topsöe prepared **lithium selenate,** $LiSeO_4.H_2O$, in small colourless crystals isomorphous with the corresponding sulphate, $LiSO_4.H_2O$. V. Lenher and E. J. Wechter obtained the salt by roasting the selenide in air, and by roasting the corresponding carbonates with selenium or selenium dioxide. The axial ratios of the monoclinic crystals are $a:b:c=1{\cdot}6022:1:0{\cdot}5442$, and $\beta=91°\ 32'$. The (101)-cleavage is complete. O. Pettersson gave 2·565 for the sp. gr.; H. Topsöe, 2·439. C. Schaefer and M. Schubert examined the ultra-red reflection spectrum. M. Born studied the pyroelectricity of this salt. According to H. Topsöe, the crystals are stable in air, and readily soluble in water. E. Mitscherlich, O. Pettersson and G. Ekman, and H. Topsöe made **sodium selenate,** Na_2SeO_4, and E. Mitscherlich found that the anhydrous salt crystallizes from its aq. soln. when the temp. exceeds 40°. V. Lenher and E. J. Wechter obtained the salt as in the case of lithium selenate; J. Meyer and K. Heider oxidized selenium dioxide by sodium dioxide, and E. Müller used an electrolytic process—*vide* selenic acid. P. Niggli gave 2·32 for the sp. gr. R. Metzner gave for the heat of formation in soln., 260 Cals., and W. G. Mixter, $(SeO_3,Na_2O)=105{\cdot}3$ Cals. C. Schaefer and M. Schubert observed the ultra-red reflection spectrum. P. Walden found the electrical conductivity of a soln. with a gram-equivalent of the salt in v litres of water at 25° to be:

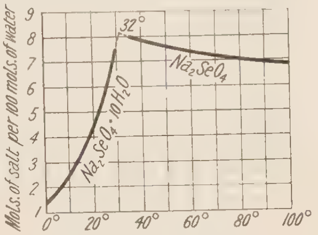


FIG. 53.—The Solubility of Sodium Selenate in Water.

v	32	64	128	256	512	1024
λ	93·5	98·9	103·8	107·2	109·9	112·5

E. Mitscherlich, C. von Hauer, and H. Topsöe observed that if the aq. soln. be allowed to evaporate spontaneously, the *decahydrate*, $Na_2SeO_4.10H_2O$, is formed in large crystals isomorphous with the corresponding sulphate. The equilibrium conditions in aq. soln. are indicated in Fig. 53, which is based on the solubility determinations of R. Funk. Representing the solubility, S, by the percentage of anhydrous salt in the soln., and S_m by the mols of anhydrous salt in 100 mols of water:

	0°	15°	25·2°	30°	25·2°	50°	75°	100°
S . .	11·74	25·01	36·91	44·05	45·47	44·49	42·83	42·14
S_m . .	1·26	3·18	5·57	7·50	7·94	7·63	7·14	6·93
Solid phase	$Na_2SeO_4.10H_2O$				Na_2SeO_4			

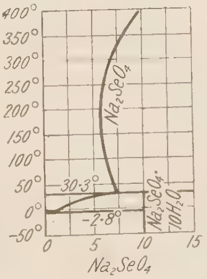


FIG. 54.—High Temperature Solubility of Sodium Selenate.

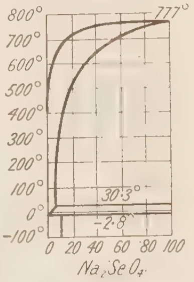


FIG. 55. — Equilibrium Curve of Sodium Selenate and Water.

There is thus a transition point at about 32°. J. Meyer and W. Aulich gave 31·8° for the transformation temp. of *selenato-Glauber's salt* to *selenato-thénardite*; and A. Smits and W. M. Mazee, 30·8°, and −2·8° with 0·2 per cent. Na_2SeO_4, for the eutectic, and they gave for the concentration, S, of a sat. soln. in molar percentages of Na_2SeO_4:

	76°	86°	107°	232°	262°
S . .	6·7	6·5	6·4	6·4	6·5

	269°	274°	333°	372°	777°
S . .	6·6	6·7	7·6	8·3	100

The results are plotted in Fig. 54. They also found the triple point to be at 777°—Fig. 55, *cf.* **1.** 10, 1, Fig. 2. H. Topsöe found that the monoclinic crystals have the axial ratios $a:b:c=1{\cdot}1059:1:1{\cdot}2384$, and $\beta=107°\ 54'$; the (100)-cleavage is complete. The sp. gr. 1·584 refers to crystals which had inclusions of the mother-liquor; and O. Pettersson found 1·603–1·621 for the sp. gr. H. Topsöe found the salt to be freely soluble in water, and to be prone to form supersaturated soln. M. Born studied the pyroelectricity of **lithium sodium selenate,** $LiNaSeO_4.6H_2O$.

E. Mitscherlich made **potassium selenate,** K_2SeO_4, by fusing selenious acid or lead selenide with potassium nitrate; V. Lenher and E. J. Wechter used the process indicated above in connection with lithium selenate; and E. Müller, the electro-oxidation process—*vide supra.* A. E. H. Tutton found that it is difficult to crystallize soln. of the alkali selenates in the open air under the ordinary moist conditions of the atm.; and he recommended crystallizing the soln. over sulphuric acid under reduced press. The potassium salt is generally deposited in large groups of much striated and distorted crystals, most frequently in irregular triplets. E. Mitscherlich said that the crystals are rhombic; H. Topsöe measured the axial ratios and A. E. H. Tutton gave $a:b:c=0·5731:1:0·7319$. H. Topsöe and C. Christiansen found the cleavage to be parallel to the (010)- and (001)-planes. The topic axes are $\chi:\psi:\omega=0·5731:1:0·7319$. E. Kochholm and N. Schönfeldt found that the rhombic crystals are isomorphous with those of potassium chromate and sulphate. The unit cell of the space lattice contains 4 mols. and has $a=7·60$ A., $b=10·40$ A., $c=6·02$ A. A. E. H. Tutton found that the optic axial angle

	Li-line.	*C*-line.	Na-line.	Th-line.	*F*-line.
$2E$ . .	145° 12′	145° 29′	146° 53′	148° 36′	150° 13′
$2H_a$ . .	70° 25′	70° 21′	70° 24′	69° 51′	69° 35′
$2H_o$ . .	93° 24′	93° 31′	92° 52′	92° 20′	91° 47′
$2V_a$ . .	76° 46′	76° 47′	76° 50′	76° 53′	76° 57′

The effect of temp. on the optic axial angle is slight. The optical character is positive. O. Pettersson gave 3·074–3·077 for the sp. gr. at 18°–21°; H. Topsöe, 3·052; P. Niggli, 3·067; and A. E. H. Tutton, 3·0657 at 20°/4°. The mol. vol. given by O. Pettersson is 71·91; by F. A. Henglein, 71·67; and by A. E. H. Tutton, 72·02. The sp. gr. of soln. with 35·76, 41·79, and 50·00 per cent. of K_2SeO_4 are respectively 1·3591, 1·3485, and 1·5590 at 20°/4°. A. F. Hallimond discussed the mol. vols. of the isomorphous series. The indices of refraction given by A. E. H. Tutton are:

			Li-line.	*C*-line.	Na-line.	Th-line.	*F*-line.	*G*-line.
Solid	17°	α . .	1·5320	1·5325	1·5352	1·5383	1·5421	1·5478
		β . .	1·5357	1·5342	1·5390	1·5421	1·5460	1·5517
		γ . .	1·5413	1·5418	1·5446	1·5478	1·5518	1·5576
	100°	α . .	1·5276	1·5281	1·5310	1·5341	1·5378	1·5440
		β . .	1·5307	1·5312	1·5340	1·5371	1·5411	1·5467
		γ . .	1·5353	1·5358	1·5387	1·5418	1·5658	1·5520
Soln.	·3596 sp. gr. .		1·3773	1·3778	1·3801	1·3819	1·3846	1·3883
	·4179 sp. gr. .		1·3861	1·3866	1·3888	1·3907	1·3936	1·3975
	·5000 sp. gr. .		1·3988	1·3992	1·4015	1·4038	1·4067	1·4105

Observations were also made by H. Topsöe and C. Christiansen. A. E. H. Tutton gave for the sp. refraction with the μ^2-formula for the *C*-line $\alpha=0·1018$, $\beta=0·1012$, and $\gamma=0·1027$; and for the mol. refraction, respectively 22·48, 22·35, and 22·67, and with the μ-formula, respectively 38·65, 38·38, and 39·05. The sp. dispersions $\mu_G-\mu_C$ are respectively 0·0024, 0·0024, and 0·0025, and the mol. dispersions respectively 0·54, 0·53, and 0·55. C. Schaefer and M. Schubert measured the ultra-red reflection spectrum. A. E. H. Tutton found that 100 grms. of water at 12° dissolve 115·0 grms. of the salt; and A. Étard gave 110·5 grms. at 0°; 112·8 grms. at 20°; and 122·2 grms. at 100°; and he represented the solubility, S, at θ° between −20° and 100° by $S=52+0·025\theta$. J. Meyer and W. Aulich gave for the percentage solubility, S:

	20°	0°	20°	40°	60°	80°	100°
S . .	51·5	51·8	52·6	53·5	54·2	54·8	55·0

where the solid is throughout K_2SeO_4. The mutual solubility curves of sodium and potassium selenates shown in Fig. 56, at 25°, give no evidence of the formation of a complex salt. A. E. H. Tutton obtained isomorphous mixtures with ammonium selenate. O. Pettersson, and A. E. H. Tutton prepared **rubidium selenate,** Rb_2SeO_4. The salt is obtained in colourless crystals by evaporating over sulphuric acid in vacuo a conc. soln. of the carbonate in selenic acid. V. Lenher and E. J. Wechter obtained rubidium selenate as in the case of the lithium salt. According to A. E. H. Tutton, the rhombic crystals have the axial ratios $a : b : c = 0{\cdot}5708 : 1 : 0{\cdot}7386$. The cleavage is like that of the potassium salt. The topic axes are $\chi : \psi : \omega = 0{\cdot}5909 : 1{\cdot}0355 : 0{\cdot}7646$. The optic axial angles are :

	Li-line.	*C*-line.	Na-line.	Th-line.	*F*-line.
$2E$ . . .	120° 25′	120° 34′	121° 20′	122° 3′	122° 49′
$2H_a$ . . .	64° 2′	63° 58′	63° 44′	63° 27′	63° 8′
$2H_o$ . . .	101° 9′	101° 0′	100° 40′	100° 11′	99° 44′
$2V_a$ . . .	68° 56′	68° 55′	68° 53′	68° 51′	68° 49′

The angle $2E$ becomes about 6° greater for 100° rise of temp. The optical character is positive. The sp. gr. is 3·8995 at 20°/4°, and the mol. vol. 80·32. P. Niggli gave 3·1902 ; O. Pettersson, 3·896–3·943 at 18°–21°, and the mol. vol. 79·97. F. A. Henglein gave 79·94. A. E. H. Tutton found that the sp. gr. of 40·60 and 47·07 per cent. soln. are respectively 1·4688 and 1·5806. A. F. Hallimond discussed the mol. vols. The refractive indices at about 20°, and 100° are :

			Li-line.	*C*-line.	Na-line.	Tl-line.	*F*-line.	*G*-line.
Solid	20°	α . . .	1·5482	1·5487	1·5515	1·5547	1·5586	1·5646
		β . . .	1·5504	1·5509	1·5537	1·5570	1·5609	1·5668
		γ . . .	1·5549	1·5554	1·5582	1·5615	1·5655	1·5715
	100°	α . . .	1·5450	1·5455	1·5478	1·5509	1·5546	—
		β . . .	1·5469	1·5474	1·5497	1·5527	1·5564	—
		γ . . .	1·5501	1·5506	1·5529	1·5560	1·5597	—
Soln.	1·4688 sp. gr. . .		1·3746	1·3750	1·3772	1·3795	1·3820	1·3860
	1·5806 sp. gr. . .		1·3842	1·3846	1·3865	1·3888	1·3915	1·3954

The sp. refraction with the μ^2-formula for the *C*-line is $\alpha = 0{\cdot}0819$, $\beta = 0{\cdot}0816$, and $\gamma = 0{\cdot}0825$; the respective mol. refractions are 25·64, 25·55, and 25·83 ; the mol. refractions with the μ-formula are respectively 44·28, 44·10, and 44·64 ; the sp. dispersions $\mu_G - \mu_C$ are all 0·0019, and mol. dispersions 0·61. The solubility at 12° is represented by the dissolution of 158·9 grms. of rubidium selenate in 100 grms. of water. A. E. H. Tutton obtained isomorphous mixtures with ammonium selenate. O. Pettersson, and A. E. H. Tutton prepared **cæsium selenate,** Cs_2SeO_4, by the method used for the rubidium salt. V. Lenher and E. J. Wechter obtained cæsium selenate as in the analogous case of lithium selenate. The axial ratios of the rhombic crystals are $a : b : c = 0{\cdot}5700 : 1 : 0{\cdot}7424$. The cleavage is like that of the potassium salt. The topic axes are $\chi : \psi : \omega = 0{\cdot}6159 : 1{\cdot}0806 : 0{\cdot}8022$. The optic axial angles are :

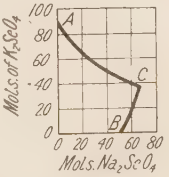


FIG. 56.—Mutual Solubilities of Sodium and Potassium Selenates.

	Li-line.	*C*-line.	Na-line.	Th-line.	*C*-line.
$2E$ . . .	135° 0′	134° 40′	132° 20′	130° 40′	128° 20′
$2H_a$ . . .	70° 68′	70° 3′	68° 9′	67° 3′	65° 9′
$2H_o$ . . .	101° 5′	101° 8′	102° 8′	103° 7′	104° 7′
$2V_a$ . . .	73° 29′	73° 7′	71° 49′	70° 18′	68° 58′

Within the range of temp. of 280°, the first median line is parallel to each of the three optic axes a, b, and c in turn ; and the plane of the optic axis crosses from $c(001)$ to $b(010)$, so that the crossing at 95° is accompanied by a temporary assumption of uniaxial properties ; the birefringence changes from negative to positive, and then from positive to negative ; the angular change in the mutual positions of the optic axis between these temp. limits is over 200°. The optical character is negative.

P. Niggli gave 4·456 for the sp. gr.; O. Pettersson, 4·34 for the sp. gr., and 94·6 for the mol. vol. A. E. H. Tutton gave 4·4528 at 20°/4° for the sp. gr., and 91·67 for the mol. vol. F. A. Henglein gave 91·09 for the mol. vol. A. F. Hallimond discussed the mol. vols. A. E. H. Tutton found the sp. gr. of soln. with 45·94 and 53·43 per cent. of the salt were respectively 1·5841 and 1·7432 at 20°. The indices of refraction were:

			Li-line.	*C*-line.	Na-line.	Th-line.	*F*-line.	*G*-line.
Solid	20°	α	1·5950	1·5955	1·5989	1·6024	1·6070	1·6138
		β	1·5960	1·5965	1·5999	1·6034	1·6080	1·6148
		γ	1·5960	1·5969	1·6003	1·6038	1·6084	1·6152
	100°	α	1·5899	1·5904	1·5939	1·5975	1·6021	—
		β	1·5901	1·5906	1·5941	1·5977	1·6023	—
		γ	1·5913	1·5918	1·5953	1·5989	1·6035	—
Soln.	1·5841 sp. gr.		1·3810	1·3814	1·3837	1·3857	1·3882	1·3919
	1·9432 sp. gr.		1·3935	1·3939	1·3962	1·3984	1·4012	1·4052

The sp. refraction with the μ^2-formula for the *C*-line are $\alpha=0·0765$, $\beta=0·0764$, and $\gamma=0·0765$, and the mol. refractions 31·25, 31·19, and 31·23 respectively; the mol. refractions with the μ-formula are 54·76, 54·63, and 54·72 respectively; the sp. dispersions $\mu_G-\mu_C$ are all 0·0019, and the mol. dispersions 0·77. For the solubility, 100 grms. of water at 12° dissolve 244·8 grms. of the salt.

A soln. of normal potassium selenate mixed with an eq. amount of selenic acid and evaporated by heat, or over conc. sulphuric acid, furnishes some tabular crystals of an acid selenate, and the mother-liquor deposits colourless crystals of **potassium hydroselenate,** $KHSeO_4$, isomorphous with the corresponding sulphate. The salt was prepared by E. Mitscherlich, J. Meyer and V. Stateczny, and H. Topsöe. The latter gave for the axial ratios of the rhombic bipyramids $a:b:c=0·8680:1:1·9375$. The optic axial angle is $2V=85°$ nearly. B. Gossner gave 2·64 for the sp. gr. J. Meyer and V. Stateczny prepared an unstable **potassium pyroselenate,** $K_2[SeO_3(SeO_4)]$, from potassium hydroselenate. It melts at 280°. J. F. Norris and W. A. Kingman obtained hygroscopic crystals of **rubidium hydroselenate,** $RbHSeO_4$, by adding to rubidium carbonate twice the amount of selenic acid necessary for neutralization. They are soluble in their weight of water; and likewise also with **cæsium hydroselenate,** $CsHSeO_4$, which furnishes large, flat plates with pointed ends, which are also very hygroscopic. G. Pellini discussed the isomorphism of rubidium hydroselenate with the hydrotellurate.

E. Mitscherlich, H. Topsöe, and R. Metzner, prepared **copper selenate,** $CuSeO_4$, from a soln. of cupric oxide or of a basic selenate in selenic acid—cupric oxide prepared by heating copper nitrate, dissolves with greater difficulty than the precipitated oxide. When the soln. is evaporated to a syrupy liquid, and cooled, it furnishes crystals which can be dried on filter-paper, and recrystallized from hot-water. V. Lenher and C. H. Kao obtained a soln. of the salt by the action of the acid on the carbonate. H. Topsöe found that the resulting blue, triclinic, prismatic crystals of the *pentahydrate*, $CuSeO_4.5H_2O$, are isomorphous with the pentahydrated sulphate; and they have the axial ratios $a:b:c=0·5675:1:0·5551$, and $\alpha=81° 58'$, $\beta=106° 34'$, and $\gamma=103° 11'$. The cleavage is not distinct; and the sp. gr. is 2·559. R. Metzner found that the heat of formation from selenic acid is 18·125 Cals., and from its elements, 135·18 Cals. The molar heat of soln. is —2·66 Cals. J. O. Perrine observed no ultra-violet fluorescence when copper selenate is exposed to the X-rays. The salt is soluble in water; a litre of the sat. soln. at 15° contains 257 grms. of salt; at 35°, 346 grms.; and at 55°, 435 grms. A soln. of the basic salt in conc. selenic acid was found by R. Metzner to yield white or colourless plates of the *dihydrate*, $CuSeO_4.2H_2O$; and the pentahydrate, at 100°, forms the *monohydrate*, $CuSeO_4.H_2O$. C. Schaefer and M. Schubert examined the ultra-red reflection spectrum. L. M. Dennis and J. P. Koller obtained **copper tetramminoselenate,** $CuSeO_4.4NH_3$, by passing ammonia through a soln. of 100 grms. of pentahydrated copper selenate in 125 c.c. aq. ammonia of sp. gr. 0·96. Clusters of deep-violet crystals were formed. The salt so obtained is the *monohydrate*, $CuSeO_4.4NH_3.H_2O$, and it can be preserved over lime, but in air it becomes dull and gives off ammonia. The salt dissolves in water, forming a deep blue soln. It becomes anhydrous when kept for 7 days over lime in a desiccator at 25 mm. press. If the monohydrate be kept 14 hrs. at 20°, and then exposed to a slow current of air at room temp. for 10 hrs. more, **copper triamminoselenate,** $CuSeO_4.3NH_3.H_2O$, is formed. The dilution of the conc. aq. soln. results in the precipitation of a basic salt. R. Metzner found that a soln., sat. at 50°, decomposes at 70°, forming **copper oxydiselenate,** $Cu(OH)_2.2CuSeO_4.nH_2O$, which when washed with cold water and dried consists of small pale green, monoclinic prisms of the *tetrahydrate,* $Cu(OH)_2CuSeO_4.4H_2O$, or $Cu(O.SeO_2.O.CuOH)_2.6H_2O$, sparingly soluble in cold water. P. Bogdan obtained the *trihydrate,* $Cu(OH)_2.2CuSeO_4.3H_2O$, or $Cu(O.SeO_2.O.CuOH)_2.3H_2O$, by heating a 10 per cent. soln. of normal copper selenate in sealed tubes at 240°–250° for several hours. It forms minute, transparent, emerald-green, prismatic crystals, insoluble in water but easily soluble in acids. When heated at about 250°, the salt loses water and decomposes with liberation of selenium. The fact that the salt does not lose water at 210° is not regarded as evidence that the water is not present in the form of water of hydration. W. Lange prepared **copper tetramminoselenate,** $CuSeO_4.4NH_3.2H_2O$; and also *copper diethyldiamminoselenate.* H. Topsöe found that a soln. of ammonium and copper selenates furnishes pale blue crystals of **ammonium copper selenate,** $(NH_4)_2Cu(SeO_4)_2.6H_2O$, which are stable in air, and isomorphous with the corresponding sulphate. The monoclinic prisms have the axial ratios $a:b:c=0{\cdot}7488:1:0{\cdot}5126$, and $\beta=105°\ 32\frac{1}{2}'$; A. E. H. Tutton gave $0{\cdot}7476:1:0{\cdot}5150$, and $\beta=105°\ 30'$, and for the topic axial ratios $\chi:\psi:\omega=6{\cdot}3868:8{\cdot}4093:4{\cdot}3308$. H. Topsöe found the (201)-cleavage to be complete. A. E. H. Tutton found for the optic axial angles at 14° :

	Li-line.	*C*-line.	Na-line.	Tl-line.	Cd-line.	*F*-line.
$2E$ . . .	91° 48′	91° 40′	90° 50′	89° 51′	89° 22′	88° 47′
$2H_a$ . .	51° 15′	51° 10′	50° 28′	49° 43′	49° 16′	48° 49′
$2H_o$ . . .	109° 41′	109° 40′	109° 32′	109° 20′	109° 13′	109° 5′
$2V_a$ . . .	55° 45′	55° 42′	55° 7′	54° 31′	54° 10′	53° 48′

The angle $2E$ increases 8° on raising the temperature from 14° to 70°. H. Topsöe found the sp. gr. to be 2·221. A. E. H. Tutton gave 52·223 at 20°/4°, for the sp. gr., and 220·64 for the mol. vol. J. A. Groshaus made some observations on this subject. The indices of refraction found by A. E. H. Tutton are :

	Li-line.	*C*-line.	Na-line.	Tl-line.	Cd-line.	*F*-line.	*G*-line.
α . .	1·5161	1·5166	1·5201	1·5235	1·5256	1·5278	1·5342
β . .	1·5304	1·5309	1·5344	1·5379	1·5402	1·4424	1·5488
γ . .	1·5347	1·5352	1·5387	1·5423	1·5446	1·5669	1·5334

H. Topsöe and C. Christiansen made some observations on this subject. A. E. H. Tutton found that at 70° the refractive indices increase by about 0·0018 for a rise of temp. of 60°. The mol. refractions for the *C*-line by the μ-formula for α, β, and γ are respectively 113·98, 118·14, and 118·09 ; and the sp. refractions by the μ^2-formula, 0·1360, 0·1390, and 0·1401 respectively ; the mol. refractions 66·71, 68·25, and 68·71 respectively ; the sp. dispersions are all $\mu_G-\mu_C=0{\cdot}0039$ and the mol. dispersions respectively 1·89, 1·91, and 1·94. C. von Hauer found that the salt cannot be dehydrated without decomposition. J. Ferguson found for the equilibrium press. for the reaction : $(NH_4)_2Cu(SeO_4)_2.6H_2O \rightleftharpoons (NH_4)_2Cu(SeO_4)_2.2H_2O+4H_2O$:

	25·°	30·6°	40·0°	50·8°	60·3°	70·4°
Press. . . .	2·8	7·5	10·6	26·3	48·5	90·8 mm.

E. Rimini and G. Malagnini made **hydrazine copper selenate,** $(N_2H_5)Cu(SeO_4)_2.\frac{1}{2}H_2O)$, isomorphous with the corresponding sulphate. It gradually decomposes when kept. R. Ripan prepared a number of copper pyridinoselenates. E. Mitscherlich prepared **potassium cupric selenate,** $K_2Cu(SeO_4)_2.6H_2O$, in a similar way. H. Topsöe showed that the monoclinic prisms have the axial ratios $a:b:c=0{\cdot}7489:1:0{\cdot}5230$, and $\beta=103^\circ\ 19'$; A. E. H. Tutton gave 0·7508 : 1 : 0·5143, and $\beta=103^\circ\ 25'$; and topic axial ratios are $\chi : \psi : \omega=6{\cdot}1819 : 8{\cdot}2338 : 4{\cdot}2347$. H. Topsöe found that the (201)-cleavage is distinct. A. E. H. Tutton gave for the optic axial angles :

	Li-line.	*C*-line.	Na-line.	Tl-line.	Cd-line.	*F*-line.
$2H_a$.	79° 33′	79° 28′	78° 56′	78° 17′	78° 3′	77° 33′
$2H_o$.	81° 33′	81° 33′	81° 33′	81° 33′	81° 33′	81° 33′
$2V_a$.	88° 49′	88° 46′	88° 27′	88° 3′	87° 55′	87° 36′

The angle $2E$ is invisible in air owing to the magnitude of the true angle. H. Topsöe found for the sp. gr. 2·527. A. E. H. Tutton gave 2·539 at 20°/4°, and for the mol. vol., 209·66. The indices of refraction are :

	Li-line.	*C*-line.	Na-line.	Tl-line.	Cd-line.	*E*-line.	*F*-line.
α .	1·5063	1·5068	1·5101	1·5132	1·5150	1·5171	1·5230
β .	1·5100	1·5195	1·5228	1·5266	1·5286	1·5308	1·5368
γ .	1·5312	1·5317	1·5349	1·5386	1·5406	1·5428	1·5391

The refractive indices diminish by about 0·0020 for a rise of temp. of 60°. H. Topsöe made some observations on the indices of refraction. A. E. H. Tutton gave for the α, β, γ axes the sp. dispersions $\mu_G-\mu_C$: 0·0031, 0·0034, and 0·0033 respectively; the mol. dispersions, 1·68, 1·77, and 1·76 respectively; the sp. refractions for the C-line and the μ^2-formula, 0·1172, 0·1196, and 0·1220 respectively; the mol. refractions 82·37, 63·69, and 64·94; and with the μ-formula, the mol. refractions 106·26, 108·92, and 111·48 respectively. The crystals are stable in air; they are sparingly soluble in water; and when the aq. soln. is heated, a green crystalline basic salt is precipitated. J. Ferguson found for the equilibrium press. of the reaction $K_2Cu(SeO_4)_2.6H_2O=K_2Cu(SeO_4)_2.2H_2O+4H_2O$:

	25·1°	32·5°	39·1°	45·1°	50·7°	61·7°
Press. . . .	11·8	21·7	36·5	55·3	79·9	137·2 mm.

A. E. H. Tutton prepared **rubidium copper selenate,** $Rb_2Cu(SeO_4)_2.6H_2O$, from a mixed soln. of theoretical proportions of the component salts in the presence of a drop of selenic acid in excess. The monoclinic, tabular crystals have the axial ratios $a : b : c=0{\cdot}7495 : 1 : 0{\cdot}5066$, and $\beta=104^\circ\ 44'$. The topic axial ratios are $\chi : \psi : \omega=6{\cdot}3179 : 8{\cdot}4295 : 4{\cdot}2704$. The cleavage parallel to the (201)-face is perfect, and that parallel to (010) is good. The optic axial angles are :

	Li-line.	*C*-line.	Na-line.	Tl-line.	Cd-line.	*F*-line.
$2E$ . .	85° 17′	85° 11′	85° 49′	86° 34′	86° 55′	87° 25′
$2H_a$ . .	48° 9′	48° 9′	48° 10′	48° 11′	48° 12′	48° 12′
$2H_o$ . .	109° 59′	109° 54′	109° 15′	108° 24′	107° 55′	107° 28′
$2V_a$ . .	52° 57′	52° 58′	53° 11′	53° 26′	53° 35′	53° 43′

The optic axial angle $2E$ increases 12° as the temp. rises up to 70°. The sp. gr. is 2·839 at 20°/4°, and the mol. vol. 219·94°. The indices of refraction are :

	Li-line.	*C*-line.	Na-line.	Tl-line.	Cd-line.	*F*-line.	*G*-line.
α .	1·5117	1·5122	1·5153	1·5185	1·5204	1·5225	1·5284
β .	1·5146	1·5152	1·5283	1·5216	1·5237	1·5257	1·5317
γ .	1·5280	1·5286	1·5318	1·5354	1·5375	1·5396	1·5461

The refractive indices decrease about 0·0020 for a 60° rise of temp. The sp. dispersion for α, β, and γ are respectively $\mu_G-\mu_C=0{\cdot}0028$, 0·0028, and 0·0030, and the mol. dispersion, 1·75, 1·77, and 1·87 respectively. The sp. refractions for the C-line and the μ^2-formula are respectively 0·1057, 0·1063, and 0·1086; and the mol. refractions 66·02, 66·35, and 67·79 respectively; and with the μ-formula, respectively 112·65, 113·32, and 116·26. J. Ferguson found for the equilibrium press. of the reaction $Rb_2Cu(SeO_4)_2.6H_2O\rightleftharpoons Rb_2Cu(SeO_4)_2.2H_2O+4H_2O$:

	28·9°	32·3°	41·1°	49·6°	59·1°	74·8°
Press. . . .	8·0	13·5	24·4	42·4	77·9	192·0 mm.

A. E. H. Tutton prepared **cæsium copper selenate,** $Cs_2Cu(SeO_4)_2.6H_2O$ as in the case of the rubidium salt. The monoclinic, prismatic crystals have the axial ratios $a:b:c=0{\cdot}7398:1:0{\cdot}4981$, and $\beta=105°\ 42'$. The topic axial ratios are $\chi:\psi:\omega=6{\cdot}4378:8{\cdot}7022:4{\cdot}3346$. The (201)-cleavage is perfect; and the (010)-cleavage is good. The optic axial angles are:

	Li-line.	*C*-line.	Na-line.	Tl-line.	Cd-line.	*F*-line.
$2E$.	77° 0′	77° 6′	77° 33′	77° 59′	78° 18′	78° 35′
$2H_a$.	44° 18′	46° 17′	44° 13′	44° 8′	44° 4′	44° 1′
$2H_o$.	114° 18′	114° 12′	113° 33′	112° 50′	112° 22′	111° 49′
$2V_a$.	48° 20′	48° 20′	48° 26′	48° 33′	48° 37′	48° 42′

The optic axial angle $2E$ changes only about 1° as the temp. rises to 75°. The sp. gr. is 3·073 at 20°/4°, and the mol. vol. is 233·79. The indices of refraction are:

	Li-line.	*C*-line.	Na-line.	Tl-line.	Cd-line.	*F*-line.	*G*-line.
α . . .	1·5243	1·5248	1·5282	1·5316	1·5335	1·5335	1·5416
β . . .	1·5259	1·5264	1·5298	1·5332	1·5352	1·5372	1·5434
γ . . .	1·5355	1·5360	1·5394	1·5427	1·5447	1·5467	1·5530

The refractive indices increase about 0·0017 for a 60° rise of temp. The sp. dispersions for α, β, and γ are respectively $\mu_G-\mu_C-0{\cdot}0027$, 0·0027, and 0·0026, and the mol. dispersions respectively 1·91, 1·93, and 1·91. The sp. refractions for the *C*-line and the μ^2-formula are respectively 0·0997, 0·0994, and 0·1015; and the mol. refractions respectively 71·62, 71·81, and 72·90; while with the mol. refractions with the μ-formula are 120·69, 123·07, and 125·31 respectively. J. Ferguson found for the equilibrium press. of the reaction $Cs_2Cu(SeO_4)_2.6H_2O \rightleftharpoons Cs_2Cu(SeO_4)_2.2H_2O + 4H_2O$:

	27·7°	36·0°	42·7°	50·0°	59·2°	65·2°
Press. . .	22·8	37·9	34·7	81·1	125·9	164·5 mm.

E. Mitscherlich obtained **silver selenate,** Ag_2SeO_4, as a white mass on treating silver carbonate with selenic acid. V. Lenher and C. H. Kao also prepared the silver salt by double decomposition of silver nitrate and calcium selenate. If the soln. in ammonia be slowly evaporated, rhombic crystals are produced, which, according to C. F. Rammelsberg, have the axial ratios $a:b:c=0{\cdot}5945:1:1{\cdot}256$. J. W. Retgers said that the rhombic pyramids are isomorphous with silver and sodium sulphates; and that they form isomorphous mixtures with sodium selenate. P. Niggli gave 5·72 for the sp. gr. E. Mulder observed no change when an electric current is passed through a sat. aq. soln. of silver selenate—0·835 grm. per litre—for 72 hrs. J. Krutwig found that chlorine does not attack silver selenate. V. Lenher and C. H. Kao said that a litre of water at 20° dissolves 1·182 grms. of silver selenate. E. Mitscherlich prepared an ammine analogous with the amminosulphate, and which therefore may be **silver tetramminoselenate,** $Ag_2SeO_4.4NH_3$. It is obtained by cooling a sat. soln. of silver selenate in warm, conc., aq. ammonia. The transparent, tetragonal crystals, according to C. F. Rammelsberg, have the axial ratio $a:c=1:0{\cdot}338$. The crystals gradually lose ammonia on exposure to air; and dissolve freely in water, and in aq. ammonia. The addition of potash-lye to the soln. precipitates fulminating silver. P. Ray and J. Dasgupta obtained **silver hexamineselenate,** $Ag_2SO_4.2(CH_2)_6N_4.12H_2O$.

V. Lenher obtained **gold selenate,** $Au_2(SeO_4)_3$, from a soln. of gold in hot, conc. selenic acid at 230°–300°—some vapour of selenium dioxide is at the same time evolved. The small, yellow crystals are decomposed by light becoming coloured dark green and bronze. They are insoluble in water; and form a reddish-yellow soln. with selenic acid; they are soluble in sulphuric and nitric acids, and with hydrochloric acid, they form chlorine, selenium dioxide, and auric chloride.

L. Michel kept a molten mixture of sodium selenate and calcium chloride with a little sodium chloride for about 2 hrs. at a dull red-heat; and, after slowly cooling, extracted the mass with water, when crystals of **calcium selenate,** $CaSeO_4$, remained. E. Mitscherlich, and C. von Hauer treated a soln. of calcium nitrate with potassium selenate, the precipitate dissolved in cold water, and separated out when the soln. was warmed. V. Lenher and C. H. Kao also obtained the salt by precipitation. D. Vorländer and W. Hempel observed no transformation of the crystals of the alkaline earth selenates into an isotropic form when heated. The acicular crystals of the *dihydrate*, $CaSeO_4.2H_2O$, so obtained are monoclinic, and isomorphous with gypsum. H. Topsöe gave 2·676 for the sp. gr.—*vide infra*. According to C. von Hauer, the salt loses 0·5 per cent. of water at 100° ; the partially dehydrated salt hardens with water like plaster of Paris ; and the salt is less soluble in hot than it is in cold water. J. Meyer and W. Aulich found the dehydration curve showed the existence of the anhydrous salt, the *hemihydrate*, $CaSeO_4.\frac{1}{2}H_2O$, the *hemitrihydrate*, $CaSeO_4.1\frac{1}{2}H_2O$; and the dihydrate ; and the percentage solubility, S, with the dihydrate as the sole stable phase, to be :

	0°	18°	30°	40°	50°	60°
S . .	7·52	7·65	6·84	6·26	5·89	5·63

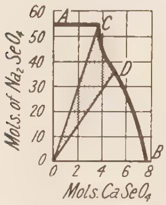


FIG. 57.—Mutual Solubilities of Sodium and Calcium Selenates.

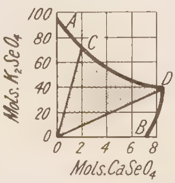


FIG. 58.—Mutual Solubilities of Potassium and Calcium Selenates.

The mutual solubility of sodium and calcium selenates is illustrated by Fig. 57 The region of stability of **sodium calcium selenate,** $Na_2Ca(SeO_4)_2.2H_2O$, is shaded in the diagram, AC is the solubility curve of $Na_2SeO_4.10H_2O$; and BD, that of $CaSeO_4.2H_2O$; and CD, that of the complex salt. The concentrations are in mols per litre at 25°. Similar remarks apply to Fig. 58 representing the mutual solubility of potassium and calcium selenates. The complex salt, **potassium calcium selenate,** $K_2SeO_4.CaSeO_4.2H_2O$, is formed. L. Michel prepared **strontium selenate,** $SrSeO_4$, by the method used for the calcium salt. V. Lenher and E. J. Wechter obtained this salt as in the case of lithium selenate, and V. Lenher and C. H. Kao obtained the salt by precipitation. L. Michel found that the rhombic crystals have the axial ratios $a : b : c = 0·7806 : 1 : 1·2892$—*vide supra*. H. Rose, and L. Michel prepared **barium selenate,** $BaSeO_4$, in a similar manner, and A. Schafarik obtained it as a white, amorphous precipitate by precipitation as in the analogous case of barium sulphate. H. Rose found that the precipitate is more prone to adsorb foreign salts than is the case with barium sulphate. V. Lenher and E. J. Wechter obtained this salt as in the case of lithium selenate ; and V. Lenher and C. H. Kao obtained the salt by precipitation. L. Michel said that the rhombic crystals have the axial ratios $a : b : c = 0·8088 : 1 : 1·3060$. F. Rinne studied the crystals of barium and strontium selenate ; and H. G. Grimm, the mixed crystals of barium selenate and potassium permanganate. A. Schafarik gave 4·67 for the sp. gr. at 20° ; P. Niggli gave 4·75 ; F. A. Henglein and R. Roth gave for the sp. gr. of barium, strontium, and calcium selenates, respectively 4·61, 4·25, and 2·88 ; L. Michel, respectively 4·75, 4·23, and 2·93 ; and F. A. Henglein and R. Roth respectively 66·9, 54·3, and 63·4 for the mol. vols. O. Pettersson found that barium selenate is not changed at dull redness, but when more strongly heated, it forms the selenite, which is stable provided reducing gases are absent. J. J. Berzelius said that at dull redness hydrogen reduces the selenate with incandescence to selenide under conditions where the sulphate is not changed ; C. Stammer found that carbon monoxide converts it at a dull red-heat into selenium and carbonate ; and H. Rose, that repeated calcinations with ammonium chloride transform it into selenium and barium chloride, and selenite. The precipitated selenate is rather more soluble in water and dil. acids than is the case with the sulphate. O. Pettersson found that 100 c.c. of cold water dissolve 0·0118 grm., and boiling water, 0·0138 grm. L. Michel found that the crystals are insoluble in water and in cold, conc. nitric acid, but slowly soluble in the hot, conc. acid. J. J. Berzelius said that it is incompletely decomposed by sulphuric acid ;

and O. Pettersson, that when boiled 10 mins. with dil. hydrochloric acid, it is completely reduced to selenite. H. Rose found that a cold, aq. soln. of sodium or potassium carbonate decomposes it completely in 24 hrs., and E. von Gerichten utilized the reaction in the purification of selenic acid. J. Meyer and W. Friedrich dissolved barium selenate in selenic acid, and found that the soln. behaved in a way analogous to a soln. of the sulphate in conc. sulphuric acid. By electrolysis, **selenatobaric acid,** $H_2[Ba(SO_4)_2]$, can be accumulated in the anode compartment; and a conc. soln. of selenic acid, sat. with barium selenate, deposits crystals of the selenatobaric acid.

A. Atterberg prepared crystals of **beryllium selenate,** $BeSeO_4.4H_2O$, from an aq. soln. of beryllium in selenic acid. H. Topsöe found that the rhombic bipyramids have the axial ratios $a:b:c=0{\cdot}9602:1:0{\cdot}9028$. The salt loses 16·63 per cent. of water at 100°; A. Atterberg said 16·90 per cent. The salt is freely soluble in water. J. J. Berzelius, and E. Mitscherlich prepared **magnesium selenate,** $MgSeO_4$, from a soln. of magnesia in selenic acid. E. Mitscherlich said that if the temp. is below 15°, prismatic crystals of the *heptahydrate*, $MgSeO_4.7H_2O$, are formed—H. Topsöe said at about 4°, and thought that the crystals are isomorphous with the heptahydrated sulphate. E. Mitscherlich said that if the temp. is over 15°, crystals of the *hexahydrate*, $MgSeO_4.6H_2O$, are formed—H. Topsöe said 6° to 8°, and added that the colourless, transparent crystals are isomorphous with the corresponding sulphate. The axial ratios of the monoclinic crystals are $a:b:c=1{\cdot}3853:1:1{\cdot}6850$, and $\beta=98°\ 32'$. The $(10\bar{1})$-cleavage is complete; and the sp. gr. is 1·928. The crystals are stable in air. A soln. of aq. proportions of ammonium and magnesium selenates furnishes transparent, well-formed tabular or prismatic crystals of **ammonium magnesium selenate,** $(NH_4)_2Mg(SeO_4)_2.6H_2O$, which, according to A. E. H. Tutton, are isomorphous with the potassium salt, and the corresponding sulphate. The isomorphous series, $R.R_2(SeO_4)_2.6H_2O$, was discussed by W. Orloff, and A. E. H. Tutton. The monoclinic prisms have the axial ratios $a:b:c=0{\cdot}7420:1:0{\cdot}4964$, and $\beta=106°\ 27'$. H. Topsöe and C. Christiansen made concordant observations. The $(20\bar{1})$-cleavage is complete. The topic axes are $\chi:\psi:\omega=6{\cdot}3299:8{\cdot}5310:4{\cdot}2365$. The optic axial angles are:

	Li-ine.	*C*-line.	Na-line.	Tl-line.	*F*-line.
$2E$ at 15° . . .	88° 12′	88° 11′	88° 4′	87° 53′	87° 25′
$2E$ at 75° . . .	76° 45′	76° 40′	76° 15′	75° 50′	75° 15′
$2H_a$	49° 48′	49° 44′	49° 6′	49° 0′	49° 20′
$2H_o$	108° 8′	108° 1′	107° 34′	107° 7′	106° 42′
$2V_a$	54° 57′	54° 55′	45° 47′	54° 33′	54° 4′

H. Topsöe gave 2·035 for the sp. gr.; P. Niggli, and A. E. H. Tutton, 2·058 at 20°/4°; the mol. vol. is 219·42. The indices of refraction are:

		Li-ine.	*C*-line.	Na-line.	Tl-line.	*F*-line.	*G*-line.
12°	α .	1·5034	1·5038	1·5070	1·5104	1·5144	1·5205
	β .	1·5056	1·5060	1·5093	1·5126	1·5166	1·5227
	γ .	1·5132	1·5136	1·5169	1·5202	1·5242	1·5305
75	α .	1·5025	1·5029	1·5062	1·5095	1·5135	—
	β .	1·5040	1·5044	1·5076	1·5108	1·5148	—
	γ .	1·5116	1·5120	1·5153	1·5187	1·5227	—

The sp. refractions by the μ^2-formula for the *C*-line are $\alpha=0{\cdot}1438$, $\beta=0{\cdot}1444$, and $\gamma=0{\cdot}1462$; and the mol. refractions respectively 64·95, 65·19, and 66·0; while with the μ-formula, the mol. refractions are 110·54, 111·02, and 112·69 respectively. The sp. dispersions $\mu_G-\mu_C$ are all 0·0040 and the mol. dispersions 1·80. C. Schaefer and M. Schubert measured the ultra-red reflection spectrum. C. von Hauer said that the salt is freely soluble in water; and that the water of crystallization cannot be expelled without decomposing the salt. J. Meyer and W. Aulich found the percentage solubility, *S*:

	0°	8°	20°	40°	60°
S	16·7	23·3	27·2	32·3	35·8
	$MgSeO_4.7H_2O$	$MgSeO_4.6H_2O$			

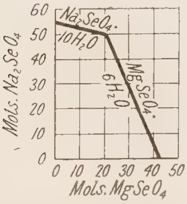


FIG. 59.—Mutual Solubility of Sodium and Magnesium Selenates.

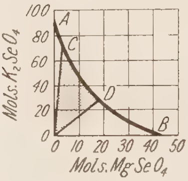


FIG. 60.—Mutual Solubility of Potassium and Magnesium Selenates.

The ice-heptahydrate eutectic is at —7·45° when 9·2 per cent. $MgSeO_4$ is in soln. The metastable soln. has the percentage solubilities of 31·2 and 32·1 at 4·7° and 7·5° respectively. There is a transition point at 8°, 23·3 per cent. $MgSeO_4$ for the transformation of the heptahydrate and hexahydrate. The dehydration curves show the existence of the monohydrate, the dihydrate, the hexahydrate, and the heptahydrate. No sodium magnesium selenate was observed to be formed by J. Meyer and W. Aulich. The mutual solubility curve of the two salts is shown in Fig. 59. The concentrations are in mols per litre at 25°. H. Topsöe, and A. E. H. Tutton prepared **potassium magnesium selenate,** $K_2Mg(SeO_4)_2.6H_2O$, as in the case of the ammonium salt. The colourless, monoclinic prisms were found by A. E. H. Tutton to have the axial ratios $a : b : c = 0·7485 : 1 : 0·5031$, and $\beta = 106° 18'$. The topic axes are $\chi : \psi : \omega = 6·2124 : 8·2998 : 4·1756$. The optic axial is $2V_a = 39° 43'$ for the Li-line; 39° 42′, for the C-line; 39° 38′, for the Na-line; 39° 34′, for the Tl-line; and 39° 25′, for the F-line. H. Topsöe gave 2·336 for the sp. gr., and P. Niggli, and A. E. H. Tutton, 2·365 at 20°/4°, and for the mol. vol., 208·60—F. A. Henglein gave 210·2. F. Ephraim studied the mol. vol. According to A. E. H. Tutton, the indices of refraction are :

	Li-line.	*C*-line.	Na-line.	Tl-line.	*F*-line.	*G*-line.
α . .	1·4936	1·4941	1·4869	1·4999	1·5035	1·5091
β . .	1·4958	1·4963	1·4991	1·5022	1·5058	1·5114
γ . .	1·5103	1·5108	1·5139	1·5172	1·5210	1·5266

The sp. refractions with the μ^2-formula and the C-line, are $\alpha = 0·1231$, $\beta = 0·1236$, and $\gamma = 0·1266$; the mol. refractions, 60·74, 60·98, and 62·48 respectively; and with the μ-formula, the mol. refractions are respectively, 103·08, 103·54, and 106·57. The sp. dispersions $\mu_G - \mu_C$ are 0·0032, 0·0032, and 0·0033 respectively, and the mol. dispersions 1·56, 1·56, and 1·62 respectively. The salt is freely soluble in water. J. Meyer and W. Aulich found that the ternary system: $MgSeO_4$–K_2SeO_4–H_2O at 25° shows the existence of the *hexahydrate*, $K_2Mg(SeO_4)_2.6H_2O$, and the *tetrahydrate*, $K_2Mg(SeO_4)_2.4H_2O$. In Fig. 60, *AC* is the solubility curve, in mols per litre at 25°, of K_2SeO_4; *BD*, that of $MgSeO_4$; and *CD*, that of the double salt, $MgSeO_4.K_2SeO_4.6H_2O$.

A. E. H. Tutton prepared **rubidium magnesium selenate,** $Rb_2Mg(SeO_4)_2.6H_2O$. The colourless monoclinic prisms have the axial ratios $a : b : c = 0·7424 : 1 : 0·5011$, and $\beta = 105° 14'$. The topic axes are $\chi : \psi : \omega = 6·2885 : 8·4705 : 4·2445$. The optic axial angle $2V_a = 47° 26'$ for the Li-line; 47° 24′, for the C-line; 47° 3′, for the Na-line; 46° 37′, for the Tl-line; and 46° 6′, for the F-line. The sp. gr. is 2·604 at 20°/4°, and the mol. vol. 218·15. F. Ephraim studied the mol. vol. The indices of refraction are :

	Li-line.	*C*-line.	Na-line.	Tl-line.	*F*-line.	*G*-line.
α . . .	1·4978	1·4983	1·5011	1·5041	1·5077	1·5133
β . . .	1·4997	1·5002	1·5031	1·5060	1·5098	1·5152
γ . . .	1·5100	1·5105	1·5135	1·5167	1·5205	1·5264

The sp. refractions with the μ^2-formula, and the C-line, are $\alpha = 0·1093$, $\beta = 0·1096$, and $\gamma = 0·1115$; the mol. refractions, 63·97, 64·18, and 65·30 respectively, and with the μ-formula, the mol. refractions are respectively 108·70, 109·12, and 111·37. The sp. dispersions $\mu_G - \mu_C$ are 0·0027, 0·0028, and 0·0029 respectively, and the mol. dispersions respectively 1·61, 1·62, and 1·70.

A. E. H. Tutton also prepared **cæsium magnesium selenate,** $Cs_2Mg(SeO_4).6H_2O$.

The colourless monoclinic prisms have the axial ratios $a:b:c=0\cdot7314:1:0\cdot4960$, and $\beta=106°\ 17'$. The topic axes $\chi:\psi:\omega=6\cdot3807:8\cdot7239:4\cdot3270$. The sp. gr. is 2·939 at 20°/4°, and the mol. vol., 231·20. F. A. Henglein gave 232·8 for the mol. vol. F. Ephraim also studied the mol. vol. A. E. H. Tutton found that the indices of refraction are :

	Li-line.	*C*-line.	Na-line.	Tl-line.	*F*-line.	*G*-line.
α . . .	1·5143	1·5148	1·5178	1·5210	1·5248	1·5304
β . . .	1·5145	1·5150	1·5179	1·5211	1·5248	1·5305
γ . . .	1·5201	1·5206	1·5236	1·5269	1·5308	1·5364

The sp. refractions with the μ^2-formula and the *C*-line are $\alpha=0\cdot1026$, $\beta=0\cdot1026$, and $\gamma=0\cdot1035$; the mol. refractions are respectively 69·70 69·72, and 70·36; and with the μ-formula, the mol. refractions are 119·02, 119·07, and 120·36 respectively. The sp. dispersions $\mu_G - \mu_C$ are 0·0026, 0·0026, and 0·0027 respectively, and the mol. dispersions 1·77, 1·75, and 1·78 respectively.

E. Mitscherlich prepared **zinc selenate,** $ZnSeO_4$, in soln. by the action of the acid on the carbonate or hydroxide, and found that when the soln. is evaporated at ordinary temp. it furnishes crystals of the *hexahydrate*, $ZnSeO_4.6H_2O$. V. Lenher and C. H. Kao also obtained a soln. of the salt by the action of the acid on the carbonate. According to H. Topsöe, the tetragonal crystals are isomorphous with the corresponding nickel sulphate, having the axial ratio $a:c=1:1\cdot895$, and the sp. gr. 2·325. H. Topsöe and C. Christiansen gave for the refractive indices :

	H-line.	*E*-line.	*D*-line.	*F*-line.
ω	1·5427	1·5367	1·5291	1·5255
ϵ	1·5165	1·5148	1·5039	1·5004

E. Mitscherlich found that if the soln. be crystallized above 30°, the *pentahydrate*, $ZnSeO_4.5H_2O$, is formed. H. Topsöe gave for the axial ratios of the triclinic crystals $a:b:c=0\cdot5829:1:05586$, and $\alpha=109°\ 21'$, $\beta=109°\ 20'$, and $\gamma=104°\ 27'$. The crystals are isomorphous with the manganese and cobalt salts. When heated to 50° some water is given off. C. Schaefer and M. Schubert studied the ultra-red reflection spectrum. H. Topsöe prepared **ammonium zinc selenate,** $(NH_4)_2Zn(SeO_4).6H_2O$, in colourless, monoclinic crystals isomorphous with the corresponding sulphate. The axial ratios are $a:b:c=0\cdot7416:1:0\cdot5062$, and $\beta=75°\ 53'$; A. E. H. Tutton gave $0\cdot7409:1:0\cdot5040$, and $\beta=73°\ 46'$. The habit is either prismatic or thickly tabular. The cleavage is parallel to $(\bar{2}01)$. The topic axes are $\chi:\psi:\omega=6\cdot2742:8\cdot4684:4\cdot2681$. H. Topsöe gave 2·200 for the sp. gr., but A. E. H. Tutton said that this is too low, the actual value is 2·261 at 20°/4°, and the mol. vol., 217·73. J. Ferguson found for the equilibrium press. of the reaction : $(NH_4)_2Zn(SeO_4)_2.6H_2O \rightleftharpoons (NH_4)_2Zn(SeO_4)_2.2H_2O+4H_2O$:

	31·3°	42·6°	48·5°	57·2°	71·3°
Press. . . .	2·9	6·9	10·1	19·9	46·5 mm.

The optic axial angles are :

	Li-line.	*C*-line.	Na-line.	Tl-line.	*F*-line.
$2E$ (20°) .	167° 30′	167° 50′	170° 0′	172° 0′	174° 30′
$2E$ (80°) .	—	131° 46′	153° 10′	154° 40′	—
$2V_a$ . . .	82° 5′	82° 5′	82° 7′	82° 9′	82° 10′
$2H_a$ . . .	74° 33′	74° 32′	74° 15′	73° 57′	73° 33′
$2H_o$ . . .	88° 11′	88° 9′	87° 41′	87° 17′	86° 44′

H. Topsöe and C. Christiansen gave $2V_a=81°\ 22'$. The indices of refraction are :

		Li-line.	*C*-line.	Na-line.	Tl-line.	*F*-line.	*G*-line.
12°	α . .	1·5201	1·5206	1·5240	1·5273	1·5316	1·5311
	β . .	1·5260	1·5265	1·5300	1·5334	1·5378	1·5443
	γ . .	1·5344	1·5349	1·5385	1·5420	1·5463	1·5529
70°	α . .	1·5189	1·5194	1·5229	1·5265	1·5308	—
	β . .	1·5246	1·5251	1·5286	1·5321	1·5364	—
	γ . .	1·5325	1·5330	1·5367	1·5403	1·5446	—

H. Topsöe and C. Christiansen made some observations on this subject. According to A. E. H. Tutton, the sp. refractions with the μ^2-formula for the C-line are α=0·1346, β=0·1359, and γ=0·1377, and the mol. refractions respectively 66·26, 66·88, and 67·77; the mol. refractions with the μ-formula are respectively 113·35, 114·63, and 116·46. The sp. dispersions $\mu_G - \mu_C$ are all 0·0038, and the mol. dispersions respectively 1·85, 1·88, and 1·89. C. Schaefer and M. Schubert examined the ultra-red reflection spectrum. E. Rimini and G. Malagnini obtained **hydrazine zinc selenate,** $(N_2H_5)_2Zn(SeO_4)_2$, from a mixed soln. of the component salts. When the white product is heated on a platinum foil, it gives off red vapours without exploding. It is sparingly soluble in water, but more soluble than the copper salt.

G. N. Wyrouboff made **potassium zinc selenate,** $K_2Zn(SeO_4)_2$, from a soln. of the component salts, and at 70°–80°, the *dihydrate*, $K_2Zn(SeO_4)_2.2H_2O$, separates out. The colourless, columnar crystals are said to be isomorphous with the corresponding ferrous and cadmium salts; and to belong to the triclinic system and to have the axial ratios $a:b:c$=0·7060 : 1 : 0·4335, and α=82° 52′, β=99° 41′, and γ=84° 46′. Twinning occurs about the $(\bar{1}01)$- and (101)-planes; and the optic axial angle $2E$=102°. H. Topsöe gave 145 for the mol. vol. A. E. H. Tutton obtained the *hexahydrate*, $K_2Zn(SeO_4)_2.6H_2O$, from a soln. of the component salts. The axial ratios of the monoclinic crystals are $a:b:c$=0·7458 : 1 : 0·5073, and β=104° 12′. The topic axial ratios are $\chi:\psi:\omega$=6·1812 : 8·2880 : 4·2045. The optic axial angle $2V_a$=66° 12′ for the Li-line; 66° 13′, for the C-line; 66° 15′, for the Na-line; 66° 17′, for the Tl-line; and 66° 20′, for the F-line. H. Topsöe and C. Christiansen gave 2·538 for the sp. gr., and the mol. vol. 212·0; A. E. H. Tutton gave the respective values 2·5580 at 20°/4°, and 208·8. F. Ephraim studied the mol. vol. J. Ferguson found the equilibrium press. of the reaction: $K_2Zn(SeO_4)_2.6H_2O \rightleftharpoons K_2Zn(SeO_4)_2.2H_2O + 4H_2O$:

	31·3°	42·6°	48·5°	57·2°	71·3°
Press. . .	23·6	50·7	75·4	120·3	218·3 mm.

The indices of refraction are:

	Li-line.	C-line.	Na-line.	Tl-line.	F-line.	G-line.
α . . .	1·5087	1·5092	1·5121	1·5151	1·5189	1·5244
β . . .	1·5146	1·5151	1·5181	1·5212	1·5252	1·5207
γ . . .	1·5297	1·5302	1·5335	1·5369	1·5410	1·5471

The optical character is positive. The sp. refractions with the μ^2-formula and the C-line are α=0·1168, β=0·1179, and γ=0·1208; and the mol. refractions 62·37, 62·98, and 64·52 respectively. The mol. refractions with the μ-formula are 106·32, 107·55, and 110·7 respectively. The sp. dispersions are respectively 0·0029, 0·0030, and 0·0032, and the mol. dispersions, 1·56, 1·59, and 1·71.

A. E. H. Tutton made **rubidium zinc selenate,** $Rb_2Zn(SeO_4)_2.6H_2O$, from a soln. of the component salts. The monoclinic prisms and plates have the axial ratios $a:b:c$=0·7431 : 1 : 0·5019, and β=105° 16′. The $(20\bar{1})$-cleavage is perfect. The topic axial ratios are $\chi:\psi:\omega$=6·2913 : 8·4662 : 4·2492. The optic axial angle $2V_a$=75° 16′ for the Li-line; 75° 14′, for the C-line; 75° 8′, for the Na-line; 75° 2′, for the Tl-line; and 74° 55′, for the F-line. The topic axial ratios are $\chi:\psi:\omega$=6·2903 : 8·4662 : 4·2492. The sp. gr. is 2·368 at 20°/4°, and the mol. vol., 218·35. F. Ephraim studied the mol. vol. According to A. E. H. Tutton, the indices of refraction are:

	Li-line.	C-line.	Na-line.	Tl-line.	F-line.	G-line.
α . . .	1·5129	1·5134	1·5162	1·5194	1·5233	1·5288
β . . .	1·5188	1·5193	1·5222	1·5253	1·5293	1·5351
γ . . .	1·5294	1·5299	1·5331	1·5365	1·5405	1·5466

The optical character is positive. The sp. refractions with the μ^2-formula and the C-line are α=0·1049, β=0·1059, and γ=0·1077, and the mol. refractions 65·67, 66·30, and 67·44 respectively. The mol. refractions with the μ-formula are 112·10, 113·39, and 115·70 respectively. The sp. dispersions $\mu_G - \mu_C$ are respectively 0·0026, 0·0027, and 0·0028; and the mol. dispersions 1·65, 1·69, and 1·76.

A. E. H. Tutton made **cæsium zinc selenate,** $Cs_2Zn(SeO_4)_2.6H_2O$, from soln. of the component salts. The axial angles of the monoclinic crystals are $a:b:c=0·7314:1:0·4971$, and $\beta=106°\ 11'$. The $(20\bar{1})$-cleavage is perfect. The topic axial ratios are $\chi:\psi:\omega=6·3710:8·7106:4·3300$. The optic axial angles $2V_a$ are 83° 33′ for the Li-line; 83° 30′, for the *C*-line; 83° 6′, for the Na-line; 82° 43′, for the Tl-line; and 82° 14′, for the *F*-line. The sp. gr. is 3·1153 at 20°/4°, and the mol. vol. 232·77. F. Ephraim studied the mol. vol. According to A. E. H. Tutton, the indices of refraction are

	Li-line.	*C*-line.	Na-line.	Tl-line.	*F*-line.	*G*-line.
α	1·5290	1·5295	1·5326	1·5358	1·5399	1·5459
β	1·5326	1·5331	1·5362	1·5394	1·5435	1·5495
γ	1·5375	1·5380	1·5412	1·5646	1·5488	1·5549

The sp. refractions with the μ^2-formula, and the *C*-line, are $\alpha=0·0989$, $\beta=0·0995$, and $\gamma=0·1002$; and the mol. refractions 71·23, 71·63, and 72·18 respectively. The mol. refractions with the μ-formula are respectively 123·19, 123·02, and 124·15. The sp. dispersions $\mu_G - \mu_C$ are 0·0025, 0·0025, and 0·0026 respectively; and the mol. dispersions 1·83, 1·83, and 1·88 respectively.

C. von Hauer prepared **cadmium selenate,** $CdSeO_4.2H_2O$, by spontaneous evaporation, or by cooling a soln. of the cadmium carbonate in selenic acid. The salt readily forms supersaturated soln. The rhombic crystals were found by H. Topsöe and C. Christiansen to be isomorphous with the corresponding manganese salt, and to have the axial ratios $a:b:c=0·9753:1:0·8764$. The (010)-cleavage is distinct. H. Topsöe gave 3·632 for the sp. gr. of the colourless, transparent crystals. C. Schaefer and M. Schubert studied the ultra-red reflection spectrum. G. N. Wyrouboff prepared a soln. of **ammonium cadmium selenate,** $(NH_4)_2Cd(SeO_4)_2$, by mixing a soln. of the component salts, and at 70°, crystals of the *dihydrate*, $(NH_4)Cd(SeO_4)_2.2H_2O$, are deposited. They are clear and colourless, and stable in air. The axial ratios of the triclinic crystals are $a:b:c=0·7277:1:0·4418$, and $\alpha=80°\ 1'$, $\beta=106°\ 9'$, and $\gamma=91°\ 34'$. The $(10\bar{1})$-cleavage is perfect, and the (001)-cleavage is not so distinct. The optic axial angle $2E=140°$. H. Topsöe gave 2·397 for the sp. gr., and 162·5 for the mol. vol. When a soln. of the component salts was crystallized at ordinary temp., colourless plates of the *hexahydrate*, $(NH_4)_2Cd(SeO_4)_2.6H_2O$, were obtained by C. von Hauer, and H. Topsöe. The monoclinic crystals have the axial ratios $a:b:c=0·7388:1:0·5001$, and $\beta=106°\ 4\frac{1}{2}'$. C. F. Rammelsberg said that the crystals are isomorphous with the corresponding sulphate. A. E. H. Tutton gave 0·7413 : 1 : 0·5026, and $\beta=106°\ 1'$. The topic axial ratios are $\chi:\psi:\omega=6·3045:8·4988:4·2715$. The optic axial angles are:

	Li-line.	*C*-line.	Na-line.	Tl-line.	Cd-line.	*G*-line.
$2V_o$.	103° 55′	103° 49′	103° 29′	103° 11′	103° 0′	102° 47′
$2V_a$.	76° 5′	76° 11′	76° 31′	76° 49′	77° 0′	77° 13′

H. Topsöe gave 2·307 for the sp. gr., and A. E. H. Tutton, 2·450 at 20°/4°, and the mol. vol., 219·99. The indices of refraction are:

	Li-line.	*C*-line.	Na-line.	Tl-line.	Cd-line.	*F*-line.	*G*-line.
α . . .	1·5167	1·5172	1·5206	1·5242	1·5262	1·4283	1·5340
β . . .	1·5221	1·5227	1·5260	1·5296	1·5315	1·5338	1·5393
γ . . .	1·5311	1·5317	1·5352	1·5386	1·5408	1·5427	1·5485

The sp. dispersions, $\mu_G - \mu_C$, for α, β, and γ are 0·0034, 0·0033, and 0·0033, and the mol. dispersions 1·81, 1·78, and 1·78. The sp. refractions for the *C*-line and the μ^2-formula are respectively 0·1235, 0·1246, and 0·1264; and the mol. refractions 66·57, 67·17, and 68·14, while for the μ-formula, the mol. refractions are 113·78, 114·99, and 116·97. H. Topsöe said that the crystals are stable in air at a low temp., but at 20°, the surface becomes matt, and a film of the dihydrate is formed. C. von Hauer, H. Topsöe, and G. N. Wyrouboff prepared crystals of **potassium cadmium selenate,** $K_2Cd(SeO_4)_2.2H_2O$, from a soln. of the component salts. The colourless, tabular, triclinic crystals are stable in air, and they have the axial ratios $a:b:c=0.7239:1:0.4614$, and $\alpha=86° 28'$, $\beta=84° 46'$, and $\gamma=101° 55'$. C. von Hauer also made observations on the crystals. The $(10\bar{1})$- and (101)-cleavages are distinct; and twinning occurs about the planes $(10\bar{1})$ and (101). The optic axial angle $2E=47°$. C. von Hauer said that the salt can be recrystallized from water without decomposition. H. Topsöe gave 3·376 for the sp. gr., and 152·0 for the mol. vol.; G. N. Wyrouboff gave respectively 3·388 at 16°, and 151·4. The *hexahydrate,* $K_2Cd(SeO_4)_2.6H_2O$, has not been prepared. A. E. H. Tutton obtained **rubidium cadmium selenate,** $Rb_2Cd(SeO_4)_2.6H_2O$, in monoclinic crystals with the axial ratios $a:b:c=0.7402:1:0.5026$, and $\beta=105° 7'$. The crystals are metastable at ordinary temp. and down to 0°, and decompose to a lower hydrate. Optical and density determinations could not be made. Holohedral, prismatic, monoclinic crystals of **cæsium cadmium selenate,** $Cs_2Cd(SeO_4)_2.6H_2O$, were obtained with the axial ratios $a:b:c=0.7319:1:0.5011$, and $\beta=106° 22'$. Owing to the rapid passage of the salt to a lower hydrated form, density and optical measurements were unsatisfactory.

C. A. Cameron and E. W. Davy added selenic acid or alkali selenate to mercurous nitrate and obtained a greyish-white, amorphous precipitate of **mercurous selenate,** Hg_2SeO_4, which blackens when exposed to light for a short time. It is sparingly soluble in water; insoluble in hydrochloric acid; and passes into mercuric selenate when boiled for a short time with nitric acid. By adding sodium selenate to a soln. of mercurous nitrate, F. Köhler[2] obtained a white precipitate which becomes yellow when washed, and a little passes into soln.—presumably by hydrolysis of the normal salt. When dried at 100° the composition is said to be that of **mercurous oxypentaselenate,** $Hg_2O.5Hg_2SeO_4$. It becomes grey when exposed to light; and when heated behaves like mercurous selenite. It is immediately blackened by potash-lye; when boiled with nitric acid it is but little attacked, and it turns white; and when heated with hydrochloric acid, selenium separates out.

According to F. Köhler, red mercuric oxide is not attacked by selenic acid; and mercuric chloride does not give a precipitate with sodium selenate. C. A. Cameron and E. W. Davy heated freshly prepared mercuric oxide with selenic acid; and evaporated the filtrate to dryness so as to drive off the excess of free acid; there remained **mercuric selenate,** $HgSeO_4$; a similar product was obtained by adding an excess of selenic acid to mercuric acetate, and treating the liquid in a similar manner. If the soln. in selenic acid be spontaneously evaporated, it furnishes white crystals which are soluble in hydrochloric and sulphuric acids; the salt is hydrolyzed by water, forming a basic salt and selenic acid. F. Köhler evaporated at a gentle heat the mother-liquor from the basic salt and obtained small, warty, yellowish-grey masses with a fibrous structure, consisting of the *monohydrate,* $HgSeO_4.H_2O$. This substance melts easily when heated, and gives off first water, and then selenium dioxide; it also furnishes mercury, mercurous selenite, and finally mercuric oxide. It forms a basic salt with mercury, and with alkali-lye it yields mercuric oxide. F. Köhler made **mercuric dioxyselenate,** $2HgO.HgSeO_4.\frac{1}{2}H_2O$, by treating freshly precipitated mercuric oxide with hot selenic acid. The same substance is produced by the action of water on the normal salt; and C. A. Cameron and E. W. Davy obtained it as a precipitate by treating mercuric acetate with a soluble selenate or selenic acid. According to F. Köhler, the product is red like basic lead chromate; but when dried in air, or at 100°, it becomes brown. When heated, it blackens and gives off water without melting; then mercury vapour, and selenium dioxide are evolved, leaving mercuric selenate behind. When heated to a still higher temp., mercuric oxide remains. It is insoluble in cold nitric acid, but soluble in the hot acid; it is freely soluble in hydrochloric acid; it forms mercuric oxide when treated with alkali-lye; and, added C. A. Cameron and E. W. Davy, it is soluble in hydrochloric, nitric, sulphuric, and selenic acids; it is sparingly soluble in water —1000 c.c. of water dissolving 0·0967 grm. They could not prepare an acid mercuric selenate. C. A. Cameron and E. W. Davy, and C. Hensgen prepared **dimercuriammonium selenate,** $(NHg_2)_2SeO_4.2H_2O$, or, according to E. C. Franklin, $(HO.Hg.NH.Hg)_2SeO_4$, **mercuric hydroxyamidoselenate,** or *selenate of Millon's base*, by dissolving mercuric dioxyselenate in conc., aq. ammonia, and adding an excess of water. The white precipitate blackens in light, and when strongly heated it gives off nitrogen, ammonia, and water vapour leaving a residue of basic mercuric selenate. It is freely soluble in hydrochloric acid, and in conc. aq. ammonia.

J. J. Berzelius[3] found that **aluminium selenate,** $Al_2(SeO_4)_3.nH_2O$, resembles the sulphate in many respects, and forms basic salts under similar conditions. J. Meyer and L. Speech showed that n is probably 10, making the formula $[Al(H_2O)_6](SeO_4)_3.4H_2O$. They made it from a warm soln. of 10 parts of aluminium chloride, $AlCl_3$, and 21 parts of sodium selenate in as little water as possible. The soln. was cooled with ice, and half its vol. of glacial acetic acid added. White crystalline aluminium selenate separated out. The washed product was purified by dissolving it in as little water as possible, precipitating with alcohol, washing with alcohol and ether, and drying in vacuo. The salt is freely soluble in water, and the acidity of the soln. shows that a little hydrolysis occurs. The salt is precipitated from its aq. soln. by alcohol, or acetic acid; and barium chloride gives a precipitate of barium selenate.

By dissolving aluminium hydroxide in an excess of selenic acid and neutralizing the excess of selenic acid with ammonia, J. J. Berzelius obtained a soln. which furnished crystals of **ammonium aluminium selenate,** $(NH_4)_2SeO_4.Al_2(SeO_4)_3.24H_2O$, or *ammonium selenatoaluminate*, $(NH_4)Al(SeO_4)_2.12H_2O$. C. Fabre obtained the salt from soln. of the component selenates. E. Wohlwill also prepared this salt. According to G. Ekman and O. Pettersson, the sp. gr. is 1·893. When heated, water is given off, then ammonia, and finally selenium oxide. C. Fabre also prepared analogous salts with methylamine, dimethylamine, trimethylamine, ethylamine, diethylamine, triethylamine, and propylamine in place of ammonia. E. Wohlwill prepared **sodium aluminium selenate,** $Na_2Al_2(SeO_4)_4.24H_2O$, or sodium selenatoaluminate, $NaAl(SeO_4)_2.12H_2O$, by crystallization from a soln. of the component salts. The octahedral crystals effloresce on exposure to air; and are freely soluble in cold water. C. Fabre prepared the salt in an analogous manner, and G. Ekman and O. Pettersson found that the sp. gr. 2·072 is less than that of the corresponding sulphate. R. Weber, E. Wohlwill, C. von Hauer, and C. Fabre made **potassium aluminium selenate,** $K_2SeO_4.Al_2(SeO_4)_3.24H_2O$, or *potassium selenatoaluminate*, $KAl(SeO_4)_2.12H_2O$, from a soln. of an eq. of selenic acid mixed with 0·25 eq. of potassium carbonate and 0·75 eq. of aluminium hydroxide. R. Weber gave 1·971 for the sp. gr. of the octahedral crystals; G. Ekman and O. Pettersson, 2·001 at 20·5°. R. Weber said that the salt intumesces when heated, and as the last of the water passes off, some selenium oxide is also given off. It is more soluble in water than ordinary alum. C. Fabre, and G. Ekman and O. Pettersson also prepared octahedral crystals of **rubidium aluminium selenate,** $Rb_2SeO_4.Al_2(SeO_4)_3.24H_2O$, or *rubidium selenatoaluminate*, $RbAl(SeO_4)_2.12H_2O$, in octahedral crystals more soluble in water than ammonium, potassium, and sodium alums. G. Ekman and O. Pettersson gave 2·137 for the sp. gr. at 18°. Similarly also with **cæsium aluminium selenate,** $Cs_2SeO_4.Al_2(SeO_4)_3.24H_2O$, or *cæsium selenatoaluminate*, $CsAl(SeO_4)_2.12H_2O$, prepared by C. Fabre, and G. Ekman and O. Pettersson. The latter found the sp. gr. to be 2·224.

L. M. Dennis and J. A. Bridgman[4] prepared **gallium selenate,** $Ga_2(SeO_4)_3.16H_2O$, when dried in air at ordinary temp., and when crystallized at room temp. it is probably a *docosihydrate*. The salt was obtained by digesting gallium hydroxide in excess in nearly boiling selenic acid for several hours; filtering off the excess of gallium hydroxide; and evaporating at room temp. The crystals are dried by suction. They show oblique extinction and are therefore monoclinic or triclinic.

The salt dissolves in water, for at 25°, 100 parts of soln. contain 57·58 grms. of gallium selenate. A mixed soln. of gallium and cæsium selenates, and selenic acid furnished crystals of **cæsium gallium selenate,** an alum of the composition $CsGa(SeO_4)_2.12H_2O$. The salt is soluble in water, so that 100 parts of soln. at 25° contain 4·15 grms. of the alum.

F. C. Mathers and C. G. Schluederberg[5] obtained **indium selenate,** $In_2(SeO_4)_3.10H_2O$, from a soln. of indium hydroxide in selenic acid. The white, hygroscopic crystals are freely soluble in water. F. Kuhlmann found that a soln. of thallous carbonate in selenic acid furnishes prismatic needles of **thallous selenate,** Tl_2SeO_4. P. S. Oettinger prepared the salt from a soln. of thallium in selenic acid. According to F. Kuhlmann, the crystals are isomorphous with thallous and potassium sulphates, and, according to J. W. Retgers, with the selenates of potassium, rubidium, and cæsium. According to A. E. H. Tutton, the holohedral, rhombic crystals are usually prismatic, rarely tabular. They have the axial ratios $a : b : c$ $=0·5551 : 1 : 0·7243$. The (100)- and (001)-cleavages are distinct. The topic axial parameters are $\chi : \psi : \omega=4·1124 : 4·0763 : 5·3189$. The optical character is negative. The optic axial angle for *C*-, Na-, and the *F*-line are respectively $2H_a$=89° 18′, 88° 45′, and 88° 20′ respectively; and $2V_a$=73° 18′, 72° 58′, and 72° 22′ respectively. The sp. gr. is 6·875. The indices of refraction are:

	Li-line.	*C*-line.	Na-line.	Tl-line.	*F*-line.
α	1·9476	1·9500	1·9640	1·9782	1·9987
β	1·9331	1·9355	1·9493	1·9635	1·9840
γ	1·9426	1·9450	1·9592	1·9737	1·9942

The sp. refractions for α, β, and γ with the *C*-ray and the μ^2-formula are 0·0703, 0·0695, and 0·0700 respectively, and the mol. refractions, 33·45, 38·05, 38·31 respectively, and with the μ-formula, 75·63, 74·47, and 75·23 respectively. The salt is sparingly soluble in cold water, but more soluble in hot water. 100 grms. of water at 9·3° dissolve 2·13 grms. of salt; at 12°, 2·4 grms.; and at 100°, 10·86 grms. Thallous selenate is therefore less soluble than the sulphate. The electrical conductivity of the aq. soln. found by E. Franke, for an eq. of the salt in *v* litres of water, at 25°, is:

v	32	64	128	256	512	1024
λ	104·3	113·2	121·0	126·4	130·0	133·4

If the thallous selenite be mixed with an excess of selenic acid, and the soln. allowed to stand in a cold place, crystals of **thallous hydroselenate,** $TlHSeO_4.3H_2O$, along with the normal salt are formed.

L. C. Lindsley and L. M. Dennis obtained **copper thallous selenate,** $Tl_2Cu(SeO_4)_2.6H_2O$, in light blue, monoclinic, prismatic crystals, from a soln. of 3 grms. of thallous selenate, and 8 grms. of copper selenate. J. Ferguson found the equilibrium press. for the reaction: $Tl_2Cu(SeO_4)_2.6H_2O \rightleftharpoons Tl_2Cu(SeO_4)_2.2H_2O + 4H_2O$:

	29·9°	40·0°	48·0°	53·9°	64·1°
Press. . . .	8·9	20·3	36·3	53·6	99·6 mm.

These two salts are members of an isomorphous series including zinc, manganese, cobalt, and nickel thallous selenates. A. E. H. Tutton gave $a : b : c$ $=0·7531 : 1 : 0·5048$, and β=104° 59′ for the axial ratios of the monoclinic crystals. The cleavage is parallel to (201); the topic axial ratios are $\chi : \psi : \omega$ $=6·3294 : 8·4045 : 4·2426$. The sp. gr. is 3·944 at 20°/4°, and the mol. vol. 218·01. The optic axial angle $2V_a$, and the indices of refraction, are:

	Li-	*C*-	Na-	Tl-	Cd-	*F*-light.
$2V_a$	85° 14′	85° 13′	85° 9′	85° 4′	85° 1′	84° 56′
α	1·6339	1·6345	1·6396	1·6461	1·6495	1·6537
β	1·6504	1·6511	1·6565	1·6631	1·6666	1·6709
γ	1·6655	1·6662	1·6720	1·6787	1·6823	1·6867

The general formula for β is $1·6353+485126\lambda^{-2}+9191500000000\lambda^{-4}+\ldots$; and for α, 1·6353 is diminished by 0·0168, and for γ, raised by 0·0154. The mol.

refractions by the μ-formula for α, β, and γ are, respectively, 138·32, 141·94, and 145·23; the sp. refractions by the μ^2-formula are, respectively, 0·0907, 0·0926, and 0·0943, while the mol. refractions are, respectively, 78·00, 79·62, and 81·08. A. E. H. Tutton prepared **magnesium thallous selenate,** $Tl_2Mg(SeO_4)_2.6H_2O$, in monoclinic crystals with the axial ratio $a:b:c=0·7485:1:0·4993$, and $\beta=105°\ 36'$. The topic axial ratios are $\chi:\psi:\omega=6·3580:8·4943:4·2412$. The cleavage is parallel to the $(\bar{2}01)$-face. The optic axial angle $2E$ is very large, while

	Li-	*C*-	Na-	Tl-	Cd-	*F*-light.
$2V_a$ . .	77° 17′	77° 20′	77° 33′	77° 50′	77° 58′	78° 10′

The sp. gr. is 3·721 at 20°/4°, and the mol. vol. 220·61. The indices of refraction are

	Li-	*C*-	Na-	Tl-	Cd-	*F*-light.
α . . .	1·6205	1·6210	1·6250	1·6297	1·6326	1·6363
β . . .	1·6292	1·6297	1·6337	1·6384	1·6414	1·6452
γ . . .	1·6359	1·6364	1·6404	1·6451	1·6482	1·6521

the general formula for β is $1·6162+504123\lambda^{-2}+4071000000000\lambda^{-4}+\ldots$; for α replace 1·6162 by 1·6075, and for γ, by 1·6229. The mol. refractions by the μ-formula for α, β, and γ are respectively 137·00, 138·92, and 140·40; and for the sp. refractions by the μ^2-formula, respectively 0·0945, 0·0956, and 0·0964, while the mol. refractions are respectively 77·59, 78·47, and 79·13. A. E. H. Tutton prepared **zinc thallous selenate,** $Tl_2Zn(SeO_4)_2.6H_2O$, in thick tabular crystals which belong to the monoclinic system, and have the axial ratios $a:b:c=0·7479:1:0·5022$; and $\beta=105°\ 54'$; A. F. G. Werther gave $0·7442:1:0·5036$, and $\beta=105°\ 51'$. The (201)-cleavage is good. Observations of the sp. gr. and the optical constants were unsatisfactory owing to the opacity, etc., of the crystals. A. E. H. Tutton gave for the topic axial ratios $\chi:\psi:\omega=6·3173:8·4468:4·2420$; and for the optic axial angles:

	Li-	*C*-	Na-	Tl-	Cd-	*F*-light.
$2V_a$ . . .	68° 12′	68° 15′	68° 34′	69° 1′	69° 14′	69° 30′
$2E$ . . .	120° 15′	120° 19′	120° 47′	121° 18′	121° 28′	121° 50′

The sp. gr. is 3·958 at 20°/4°; and the mol. vol. 217·69. The indices of refraction are:

	Li-	*C*-	Na-	Tl-	Cd-	*F*-light.
α . .	1·6352	1·6358	1·6414	1·6479	1·6520	1·6576
β . .	1·6475	1·6481	1·6539	1·6606	1·6648	1·6706
γ . .	1·6549	1·6556	1·6615	1·6687	1·6731	1·6793

The formula for β is $1·6271+825988\lambda^{-2}+41081000000000\lambda^{-4}\ldots$; and for α, the constant 1·6271 is reduced by 0·0125, and for γ, increased by 0·0076. The mol. refractions by the μ-formula for α, β, and γ are respectively 138·41, 141·08, and 142·70; the sp. refractions by the μ^2-formula, respectively 0·0905, 0·0919, and 0·0928, and the mol. refractions, respectively 78·02, 79·22, and 79·93. C. Fabre prepared colourless octahedral crystals of **thallous aluminium selenate,** $Tl_2SeO_4.Al_2(SeO_4)_3.24H_2O$, or *thallous selenatoaluminate*, $TlAl(SeO_4)_2.12H_2O$, from a mixed soln. of the component salts. J. Meyer found that thallic oxide and selenic acid furnish two salts, **thallic hydroxyselenate,** $Tl(OH)SeO_4.H_2O$, and **thallic hydroselenate,** $TlH(SeO_4)_2.2H_2O$. The transformation point from one to the other is at 45°. J. Meyer and H. Wilk treated thallic hydroxide with a sat. soln. of ammonium selenate, which, when treated with ammonia and alcohol at 0°, yields **thallic amminoselenate,** $[Tl(H_2O)_6(NH_3)_2]_2(SeO_4)_3$, which is stable only in an atm. of ammonia. They also prepared colourless thallosic selenate, $Tl_2SeO_4.Tl_2(SeO_4)_3$, and yellow $5Tl_2SeO_4.Tl_2(SeO_4)_3$. V. Fortini prepared crystals of **potassium thallic selenate,** $K_2SeO_4.Tl_2(SeO_4)_3.8H_2O$, or *potassium selenatothallate*, $KTl(SeO_4)_2.4H_2O$, from a mixed soln. of thallic selenate and potassium selenate evaporated in vacuo. The crystals are soluble in dil. acids, and resemble the corresponding sulphates.

S. Jolin prepared **cerous selenates,** $Ce_2(SeO_4)_3.nH_2O$, with 6, 9, and 12 mols of water of crystallization, and M. Cingolani with 4, 5, 7, 8, 10, 11, and 12 mols.

M. Cingolani made the rough exploration of the solubility curve shown in Fig. 61. The breaks in the curve represent transition points of the different hydrates. The anhydrous selenate was obtained by heating one of the hydrates to 180°; and it then appears as a fine-grained, white, amorphous powder which begins to lose acid vapours at about 200°. The *tetrahydrate*, $Ce_2(SeO_4)_3.4H_2O$, was obtained by mixing 14·1 grms. of cerous nitrate in 50 c.c. of water with a soln. of 49·11 grms. of selenic acid in 100° c.c. of water; when the soln. is heated to the b.p. prismatic crystals of the tetrahydrate then separate. The hexagonal prisms belong to the rhombic system, and have the axial ratios $a:b:c=0·6834:1:—$. The *pentahydrate*, $Ce_2(SeO_4)_3.5H_2O$, is obtained from a soln. of the tetrahydrate containing an excess of selenic acid. S. Jolin's *hexahydrate* was not obtained by M. Cingolani, but he obtained the *heptahydrate*, $Ce_2(SeO_4)_3.7H_2O$, by keeping a 40 per cent. soln. of the tetrahydrate at about 80·5°; and the *octohydrate*, $Ce_2(SeO_4)_3.8H_2O$, at 60° to 78°; the *decahydrate*, $Ce_2(SeO_4)_3.10H_2O$, at 34° to 46°; the *henahydrate*, $Ce_2(SeO_4)_3.11H_2O$, at 12° to 28°; the *dodecahydrate*, $Ce_2(SeO_4)_3.12H_2O$, at about 0°. The dodecahydrate was also prepared by S. Jolin. M. Cingolani could not prepare S. Jolin's *enneahydrate*.

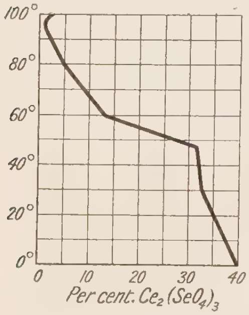


FIG. 61.—Solubility of Cerous Selenate in Water.

H. Topsöe prepared **enneahydrated yttrium selenate,** $Y_2(SeO_4)_3.9H_2O$, in colourless, transparent, six-sided plates belonging to the rhombic system, and with the axial ratios $a:b:c=1·0686:1:0·5760$; twinning occurs parallel to the (100)-plane; and the (100)-cleavage is well defined. The sp. gr. is 2·780. Pale red, tabular, rhombic crystals of **enneahydrated erbium selenate,** $Er_2(SeO_4)_3.9H_2O$, with the axial ratios $a:b:c=1·0752:1:0·5168$, were similarly prepared. The cleavage is parallel to the (100)-plane. The crystals are isomorphous with the yttrium salt. The sp. gr. is 3·171. Colourless, monoclinic crystals of **octohydrated yttrium selenate,** $Y_2(SeO_4)_3.8H_2O$, were also obtained in colourless, tabular, monoclinic crystals of sp. gr. 2·895; likewise yellowish-red monoclinic crystals of **octohydrated erbium selenate,** $Er_2(SeO_4)_3.8H_2O$, with the axial ratios $a:b:c=3·0218:1:2·0012$, and $\beta=61° 15'$. The sp. gr. is 3·516. These two salts are isomorphous with **octohydrated didymium selenate,** $Di_2(SeO_4)_3.8H_2O$, also obtained in reddish, columnar, monoclinic crystals of sp. gr. 3·239. P. T. Cleve obtained **hexahydrated lanthanum selenate,** $La_2(SeO_4)_3.6H_2O$, crystallized from a warm soln., and the *decahydrate*, by spontaneous evaporation; a soln. of this salt and potassium selenate furnished crystals of **potassium lanthanum selenate,** $KLa(SeO_4)_2.4\frac{1}{2}H_2O$, stable in dry air. Flattened prisms of **ammonium lanthanum selenate,** $(NH_4)La(SeO_4)_2.4H_2O$, were likewise obtained; and a white crust, **sodium lanthanum selenate,** $NaLa(SeO_4)_2.2H_2O$, which retains its water of crystallization in vacuo over sulphuric acid. J. A. N. Friend and A. A. Round prepared **neodymium selenate,** $Nd_2(SeO_4)_3$, together with the corresponding *pentahydrate*, and *octohydrate*, as well as a possible *dodecahydrate*. P. T. Cleve found that when a soln. of **octohydrated samarium selenate,** $Sm_2(SeO_4)_3.8H_2O$, is evaporated over sulphuric acid at 18°, sulphur-yellow crystals are obtained. The salt is soluble in water; at about 10°, the *dodecahydrate* is formed. No complex salt with sodium has been found, but **potassium samarium selenate,** $K_2Sm(SeO_4)_2.3H_2O$, and **ammonium samarium selenate,** $(NH_4)_2Sm(SeO_4)_3.3H_2O$, form sulphur-yellow crystals when the aq. soln. is evaporated spontaneously.

A. Ditte[6] prepared **titanyl selenate,** $(TiO)SeO_4.H_2O$, or $TiO_2.H_2SeO_4$, by a method analogous to that employed for the stannyl compound—*vide infra.* H. Brenek also prepared a similar compound by boiling a soln. of α-titanic acid in hot dil. sulphuric acid mixed with an eq. of selenic acid; when half this amount of selenic acid is employed, the oxyselenate, $2TiO_2.SeO_3.H_2O$, or **titanyl dihydroxy-**

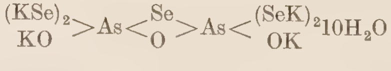
selenate, $(TiO)_2(HO)_2SeO_4$, is formed. A. Ditte prepared **zirconyl selenate,** $(ZrO)SeO_4.H_2O$, by the method used for stannyl selenate (*q.v.*). M. Weibull obtained **zirconium selenate,** $Zr(SeO_4)_2.4H_2O$, by the spontaneous evaporation of a soln. of zirconium hydroxide in selenic acid. The 4-sided, and 6-sided plates belong to the hexagonal system. The salt loses 3 mols. of water at 100°, and the fourth mol. at 120°–130°. The anhydrous salt is a little hygroscopic. It is soluble in water; and sparingly soluble in alcohol, and conc. acids. When the aq. soln. is boiled, a basic salt is precipitated. P. T. Cleve[7] prepared **enneahydrated thorium selenate,** $Th(SeO_4)_2.9H_2O$, by evaporating a soln. of thorium hydroxide in dil. selenic acid; G. N. Wyrouboff used a small excess of selenic acid, evaporated the soln. at 35°–50°, and washed the product with alcohol. H. Topsöe said that the monoclinic, prismatic crystals have the axial ratios $a:b:c=0{\cdot}5984:1:0{\cdot}6542$, and $\beta=98°\ 26'$. The (010)-cleavage is complete, and the (001)-cleavage distinct; twinning occurs about the (100)-plane. The salt is isomorphous with the corresponding sulphate, and the sp. gr. is 3·026. R. Thalén made some observations on the crystals. P. T. Cleve found that the crystals lose 8 mols. of water at 120°–190°—G. N. Wyrouboff said 250°—and the rest at 400°. The salt is decomposed into thoria at about 1500°. P. T. Cleve said that 100 parts of water dissolve 0·5 parts of salt at 0°, and 2 parts at 100°. G. N. Wyrouboff said that the solubility is about one per cent. When a soln. of the salt in sodium selenate soln. is cooled, C. Manuelli and M. Cingolani said that colourless, monoclinic crystals of the *octohydrate*, $Th(SeO_4)_2.8H_2O$, are formed. G. N. Wyrouboff said that the isomorphism of the salt indicates that it is enneahydrated not octohydrated. A. Rosati gave for the axial ratios of the monoclinic crystals of the octohydrate $a:b:c=0{\cdot}6037:1:0{\cdot}6712$, and $\beta=81°\ 40'$.

A. Ditte[8] prepared **stannyl selenate,** $(SnO)SeO_4.H_2O$, or $SnO_2.H_2SeO_4$, by dissolving gelatinous stannic acid in warm selenic acid, and evaporating the soln. to a syrupy liquid. On cooling, transparent, rhomboidal lamellæ or hexagonal prisms are obtained. This compound is produced in the presence of a large excess of selenic acid. The crystals are hygroscopic, and are decomposed by an excess of water with the separation of stannic hydroxide.

E. Mitscherlich prepared **lead selenate,** $PbSeO_4$, as a white powder, by adding a soln. of lead nitrate to sodium selenate; V. Lenher and C. H. Kao used a similar process; A. Schafarik likewise obtained it as a white, crystalline powder. F. C. Mathers and F. V. Graham obtained lead selenate by the action of lead dioxide or selenium dioxide at 100°. L. Michel obtained crystals isomorphous with anglesite by melting the amorphous precipitate with a mixture of potassium and sodium nitrates at 300° for 2 hrs., and after slowly cooling, lixiviating the mass with water; he also obtained the crystals by melting lead chloride with a mixture of alkali selenate and sodium chloride. The mineral *kerstenite*, mentioned in connection with lead selenite, may be regarded as a lead selenate which is probably isomorphous with anglesite. A. Schafarik gave 6·37 for the sp. gr. at 22°; and when melted it loses oxygen, passing into the selenite. C. A. Cameron and J. Macallan found that when the salt is heated, selenium dioxide is evolved. F. C. Mathers found that a layer of the selenate on a platinum dish as cathode, with dil. selenic acid as electrolyte, is partially reduced. H. Fonzes-Diacon found lead selenate to be more stable when heated than most of the other metal selenates, so that the temp. necessary for reducing the salt to lead selenide by means of hydrogen can be attained without losing much selenium dioxide; carbon reduces the salt more easily than is the case with lead sulphate; and aluminium powder reduces the selenate with explosive violence, forming aluminium selenide. A. Ditte found that the action of hydrochloric acid, sodium chloride, and potassium iodide on lead selenate resembles their action on the sulphate. F. C. Mathers and R. S. Bonsib found that a soln. of ammonium carbonate converts the salt, in the cold, into lead carbonate and ammonium selenate. If basic lead acetate be added to a soln. of sodium selenate, C. T. Barfoed obtained crystals of **lead oxyselenate,** $PbO.PbSeO_4$, which, when treated with acetic acid, form the normal salt. According to D. Strömholm, if lead hydroxide be added to $0{\cdot}066N$-$(NH_4)_2SeO_4$, until the soln. is free from selenic acid, a white, voluminous, crystalline mass of **lead dioxyselenate,** $2PbO.PbSeO_4.H_2O$, is formed. When heated, it becomes pale yellowish-red.

E. Szarvasy[9] obtained **sodium orthoselenoarsenate,** $Na_2AsSe_4.9H_2O$, together with selenotrioxyarsenate, when arsenic pentaselenide is dissolved in soda-lye. It crystallizes in ruby-red needles, which rapidly lose their water of crystallization when exposed to the air; it is readily soluble in water, and the soln. readily undergoes decomposition, selenium being deposited. Mineral acids precipitate arsenic pentaselenide from its alkaline soln. in the form of a reddish-brown flocculent precipitate. W. Muthmann and A. Clever prepared **potassium metaselenoarsenate,** $KAsSe_3.2H_2O$, by adding arsenic pentaselenide to a soln. of selenium in potash-lye, and, after the mixture had been heated some time, filtering into alcohol, and adding a small proportion of water in order to dissolve other compounds which are formed at the same time, and the product was then dried on a porous plate. It crystallizes in reddish-yellow prisms, and is easily soluble in hot water, but the soln. soon decomposes, with the deposition of selenium; alkaline soln. are somewhat more stable. Acids precipitate arsenic pentaselenide from the aq. soln. with the evolution of hydrogen selenide. With lead and silver salts, it gives a black precipitate; with barium salts, a reddish-white precipitate, which rapidly decomposes. E. Szarvasy, and R. F. Weinland and O. Rumpf, prepared **sodium trioxyselenoarsenate,** $Na_3AsO_3Se.12H_2O$, or $Se{=}As(ONa)_3$, by dissolving arsenic pentaselenide in soda-lye, but as the soln. readily decomposes when exposed to the air, it is necessary to work in an atm. of hydrogen. The salt may be obtained as colourless crystals on the addition of methyl alcohol to the aq. soln.; the crystals, when left exposed to the air, lose their water of crystallization and turn red, owing to the liberation of selenium. The rhombic crystals are isomorphous with the corresponding trioxysulphoarsenate, and have the axial ratios $a:b:c=0{\cdot}9284:1:0{\cdot}6409$. Acids decompose the salt, giving a red precipitate while arsenic trioxide remains in soln. Silver and lead salts precipitate the corresponding selenide.

W. Muthmann and A. Clever prepared **sodium octoxytriselenodiarsenate,** $3Na_2Se.3Na_2O.As_2O_5.50H_2O$, or $Na_{12}As_2O_8Se_3.50H_2O$, by warming arsenic pentaselenide with a conc. soln. of sodium hydroxide; a hydrate of sodium monoselenide is at first precipitated, but on filtering, and mixing the filtrate with alcohol, the oxy-compound crystallizes out in white, elongated prisms, which are fairly stable on exposure to air. It is easily soluble in water; acid precipitates selenium from the soln. and an arsenic selenide is not formed. With lead and silver salts, it gives a black precipitate; and with barium chloride, a white, amorphous precipitate which is easily soluble in warm water. C. Messinger assumed that the compound contained 58 mols. of water of crystallization. W. Muthmann and A. Clever prepared **potassium trioxypentaselenodiarsenate,** $K_6As_2O_3Se_5.10H_2O$, or



$$\begin{matrix}(KSe)_2\\KO\end{matrix}{>}As{<}\begin{matrix}Se\\O\end{matrix}{>}As{<}\begin{matrix}(SeK)_2\\OK\end{matrix}10H_2O$$

analogous to the corresponding sodium trioxypentasulphoarsenate (*q.v.*). The trioxypentaselenodiarsenate is obtained by gradually adding 5 grms. of arsenic pentasulphide to a conc. soln. of 10 grms. of potassium hydroxide, while the mixture is cooled with ice. The liquid is filtered into 300 c.c. of absolute alcohol, and the orange-red, crystalline mass is washed rapidly with alcohol, and dried on a porous tile. It rapidly decomposes and darkens on exposure to air, and moisture, selenium being deposited; it dissolves easily in water, forming a greenish-yellow soln., and then decomposes rapidly with the deposition of red selenium. With salts of the heavy metals it gives dark, amorphous precipitates; with barium salts, a reddish-white compound, which decomposes very rapidly. When treated with acids, it yields arsenic pentaselenide.

According to R. F. Weinland and G. Barttlingck, if a soln. of selenic acid, arsenic acid, and potassium hydroxide in the molar proportions 1 : 2 : 2 be evaporated on a water-bath, crystals of **potassium selenatoarsenate,** $2K_2O.2SeO_3.As_2O_5.3H_2O$, or $KH_2AsO_4.KHSeO_4$, are formed in colourless, rhombic plates; and similarly also with **rubidium selenatoarsenate,** $2Rb_2O.2SeO_3.As_2O_5.3H_2O$; and with **ammonium selenatoarsenate,** $2(NH_4)_2O.2SeO_3.As_2O_5.3H_2O$. If the proportions indicated above be 1 : 4 : 1, colourless prisms of **potassium pentaselenatodiarsenate,** $3{\cdot}5K_2O.0{\cdot}5SeO_3.As_2O_5.5{\cdot}5H_2O$, or else $2KH_2AsO_4.5KHSeO_4.H_2O$, are formed.

C. A. Cameron and J. Macallan obtained **antimony selenate** as a white, crystalline mass, by dissolving antimony in hot selenic acid, and heating the liquid to drive off the excess of acid. The white mass consists of microscopic prismatic crystals which are neither decomposed nor dissolved by boiling water; they dissolved in hot selenic acid without forming an acid salt. They are only slightly soluble in other acids. G. Hofacker melted a mol of antimony selenide, 1·5 grm. atoms of selenium, and 3 mols of sodium carbonate mixed with carbon at a high temp.; he extracted the mass with boiling water; and dissolved in the liquor a gram-atom of selenium. The filtered soln. was evaporated for crystallization, or treated with alcohol whereby crystals of **sodium selenoantimonate,** $Na_3SbSe_4.9H_2O$, isomorphous with the corresponding sulphantimonate, were obtained. Large crystals appear orange-yellow and small ones, colourless. When heated, the salt melts in its water of crystallization, and at a higher temp. forms a brown mass, which then decomposes with the evolution of selenium. When heated at a low temp. in dry air it loses water and selenium. It is more sensitive to air than the sulphantimonate, and is rapidly coloured hyacinth-red. 100 grms. of water dissolve 50 grms. of salt at 12°; the dil., aq. soln., protected from air, slowly deposits grey plates, and sodium selenite remains in soln. Acids precipitate antimony pentaselenide incompletely from the aq. soln. Lead acetate, and sulphates of copper, iron (ous), nickel, and cobalt give black precipitates; mercuric chloride and mercurous acetate, brownish-black precipitates; zinc sulphate, a red precipitate; cadmium chloride, a reddish-brown precipitate; and manganese sulphate, a brown precipitate. Silver nitrate gives an impure precipitate of **silver selenatoantimonate,** Ag_3SbSe_4. By treating a soln. of bismuth carbonate in a similar manner, J. A. Cameron and J. Macallan obtained **bismuth selenate** in small, colourless, prismatic crystals, insoluble in water; and not decomposed by boiling water. The salt is soluble in selenic acid, hot sulphuric acid, and in nitric and hydrochloric acids; and it is decomposed by alkali-lye.

According to W. Prandtl and F. Lustig,[10] a soln. of **vanadatoselenic acid,** or **selenatovanadic acid,** $3V_2O_5.4SeO_2.4H_2O$, is produced by dissolving vanadium pentoxide in selenic acid. The soln., conc. on the water-bath, is yellowish-brown. G. Gain found that by dissolving hydrated hypovanadic acid, $V_2O_4.2H_2O$, in dil. selenic acid, a blue liquid is produced which, on evaporating for 15 days in vacuo, deposits bright blue, deliquescent, crystalline **hypovanadic selenate,** $V_2O_4.3{\cdot}5SeO_3.7H_2O$; and if an excess of selenic acid is used, a blue, still more deliquescent salt, $V_2O_4.5SeO_3.10H_2O$, is obtained. These salts differ from the corresponding sulphates, only in the proportion of water. J. Meyer and E. Markowicz found that in the electrolytic reduction of vanadic salts in the presence of selenic acid, the latter is also reduced, and that attempts to prepare vanadium selenium alum, or vanadium selenate, were not successful. A red *vanadium acetoselenate,* $V_2(CH_3.COO)(SeO_4)_4.nH_2O$, was obtained by adding selenic acid to a conc. soln. of vanadium acetate. The greenish-white precipitate was quickly washed and dried in an atm. of carbon dioxide.

R. Metzner[11] obtained **tellurium selenate,** $2TeO_2.SO_3$, from a soln. of tellurium dioxide in boiling sulphuric acid. C. Fabre prepared a soln. of **chromic selenate,**

$Cr_2(SeO_4)_3$, as in the case of chromic sulphate. J. Meyer and V. Stateczny found that selenic acid dissolves chromic acid at 23° :

Selenic acid, H_2SeO_4	55·1	81·2	87·9	96·2	98·5	per cent.
Chromic acid, CrO_3	8·65	0·16	0·29	0·17	0·35	,,

They obtained **chromatoselenic acid,** H_2CrSeO_7, by the action of 20 grms. of chromic acid on 50 grms. of 9·8 per cent. selenic acid. The orange precipitate melts at 200°–205° to a dark wine-red liquid, which, when further heated, gives off oxygen. It is only sparingly soluble in conc. sulphuric acid; and insoluble in carbon disulphide, carbon tetrachloride, and chloroform. It is readily reduced by organic and inorganic compounds to form chromic salts and selenium dioxide. Alcohol is immediately inflamed; and a mixture of sugar and potassium chloride explodes vigorously in contact with a drop of chromatoselenic acid Eq. proportions of potassium selenate and chromic anhydride form **potassium chromatoselenate,** K_2CrSeO_7, or $K_2[CrO_3(SeO_4)]$, when heated in a sealed tube on a water-bath. The salt melts at 138°, and resembles potassium chromatosulphate. The corresponding **barium chromatoselenate,** $BaSeCrO_7$, or $Ba[CrO_3(SeO_4)]$, was prepared in a similar way. When heated, it decomposes before melting. J. Meyer and L. Speich prepared violet chromic selenate, $[Cr(H_2O)_6]_2(SeO_4)_3.3$ or $4H_2O$, by adding selenic acid to a cold soln. of violet chromic nitrate, and adding alcohol. The salt is freely soluble in water, from which it is precipitated by alcohol or acetic acid. Its aq. soln. dissolves chromic hydroxide with formation of green basic salts. When the violet salt is heated in soln. or in the solid state at 90°, it changes irreversibly into a green chromiselenate. The green salt prepared in the solid state has the composition $Cr_2(SeO_4)_3.10H_2O$, and dissolves very slowly in water, probably only after addition of water. The green salt may have a constitution of the type $[Cr(SeO_4)(H_2O)_3]_2SeO_4$. When a soln. of the violet salt is boiled for some time, a green compound is formed which is precipitated by alcohol as a green oil and dries to an amorphous green solid. It is very soluble in water and gives no precipitate with barium salts or with ammonia. It is probably **triselenatochromic acid,** $H_3[Cr(SeO_4)_3]$.

C. Fabre found that when a soln. of chromic selenate is mixed with ammonium selenate, the violet soln. deposits octahedral, reddish-violet crystals of **ammonium chromic selenate,** $(NH_2)_2SO_4.Cr_2(SeO_4)_2.24H_2O$, or *ammonium selenatochromate,* $NH_4Cr(SeO_4)_2.12H_2O$. O. Pettersson said that the sp. gr. is 1·984 at 26°. C. Fabre added that the violet soln. becomes green at 55°–60°. The green soln. crystallizes only when allowed to evaporate spontaneously for several months. The corresponding salts with ethylamine and propylamine in place of ammonia were prepared. The ammonium chromic alum so obtained is a type of the *chromium-selenium alums,* analogous to the aluminium-selenium alums, and the alums proper. C. Fabre likewise prepared **sodium chromic selenate,** $Na_2SeO_4.Cr_2(SeO_4)_3.24H_2O$, or *sodium selenatochromate,* $NaCr(SeO_4)_2.12H_2O$; **potassium chromic selenate,** or *potassium selenatochromate,* $KCr(SeO_4)_2.12H_2O$. The latter salt was made by E. Wohlwill; and O. Pettersson gave 2·078 for the sp. gr. at 173°. H. Sauer, and G. Joos studied the absorption spectrum of the crystals. C. Fabre prepared in a similar manner **rubidium chromic selenate,** or *rubidium selenatochromate,* $RbCr(SeO_4)_2.12H_2O$, which, according to O. Pettersson, has the sp. gr. 2·219 at 17·9. H. Sauer examined the absorption spectrum. C. Fabre likewise prepared **cæsium chromic selenate,** or *cæsium selenatochromate,* $CsCr(SeO_4)_2.12H_2O$; H. Sauer examined the absorption spectrum. C. Fabre prepared **thallous chromic selenate** or *thallous selenatochromate,* $TlCr(SeO_4)_2.12H_2O$, in deep violet crystals, almost black by reflected light. O. Pettersson gave 576·6 for the mol. vol. H. Sauer examined the absorption spectrum.

J. Meyer and L. Speich prepared **chromic chloropentaquoselenate,** $[Cr(H_2O)_5Cl]SeO_4.3H_2O$, by treating the corresponding chromic chloride with sodium selenate; it furnishes a green powder freely soluble in water, and alcohol. Other chloroselenates corresponding with the known chlorosulphates were not successfully prepared. They also prepared **chromic dichlorotetraquohexaquoselenate,** $[CrCl_2(H_2O)_4](SeO_4)_2[Cr(H_2O)_6]$, from a soln. of 4 parts of chromic dichlorotetraquochloride, and 10 parts of violet chromic chloride. It is a green, crystalline powder freely soluble in water, and sparingly soluble in alcohol. No complex salts of the type $[CrCl_2(H_2O)_4](SO_4)_2M(H_2O)_6]$ were prepared. They obtained **chromic hexamminoselenate,** $[Cr(NH_3)_6](SeO_4)_3$, from the corresponding nitrate and selenic acid. It is precipitated from its aq. soln. by alcohol as a heavy, crystalline powder. This salt is amorphous, the corresponding sulphate is pentahydrated. Silver selenate and chromic chloropentamminochloride furnish **chromic chloropentamminoselenate,** $[CrCl(NH_3)_5]SeO_4$, as a heavy, red, amorphous powder sparingly soluble in water; the corresponding sulphate is dihydrated. Chromic hexacarbamidochloride and silver selenate give **chromic hexacarbamidoselenate,** $[Cr(NH_2.CO.NH_2)_6]_2(SeO_4)_3$. The green crystalline powder is soluble in water, and is precipitated from its aq. soln. by alcohol; and **chromic trisethylenediamidoselenate,** $[Cr\,en_3]_2(SeO_4)_3$, was obtained as a reddish-yellow crystalline powder from the corresponding chloride and silver selenate. It is soluble in water; and is precipitated by alcohol from its aq. soln.

E. Wendehorst digested a mixture of selenic and molybdic acids on a water-bath for several days, and on evaporating the liquid layer, obtained a crystalline mass of **selenatomolybdic hexoxide,** $SeO_3.MoO_3$. When this product is mixed with a little water, and dried at 110°, it furnishes the *dihydrate*, $SeO_3.MoO_3.2H_2O$. No other hydrate was obtained. Titration with potassium hydroxide, using phenolphthalein as indicator, shows that the dihydrate is a tetrabasic **selenatomolybdic acid,** H_4SeMoO_8. The acid is hygroscopic; it gives a blue colour with alcohol, and ordinary acetone, but purified acetone gives no such effect. Potassium permanganate does not react with the acid, but with hydrogen dioxide, the orange colour of a permolybdate is produced.

According to R. Sendtner,[12] uranium tritoctoxide dissolves with difficulty in selenic acid, whereas uranyl hydroxide is readily dissolved. He reported **uranyl selenate,** $(UO_2)SeO_4.nH_2O$, to be formed as a gummy mass by evaporating on the water-bath a soln. of uranyl hydroxide in selenic acid; it can be dried in a desiccator. If a soln. of uranyl hydroxide in hot selenic acid be evaporated on a water-bath to a syrupy consistency, and the acid soln. allowed to stand a few days at 0°–4°, a pale yellow, deliquescent mass of **uranyl hydroselenate,** $(UO_2)H_2(SeO_4)_2.18H_2O$, is formed; as well as greenish-yellow needles of **uranyl hydrotriselenate,** $(UO_2)_2H_2(SeO_4)_3.18H_2O$. There is nothing to show that all these products are not really mixtures. T. Sendtner also prepared yellow crystalline masses of **ammonium uranyl selenate,** $(NH_4)_2(UO_2)(SeO_4)_2.2H_2O$, from a soln. of ammonium uranate in dil. selenic acid; or by adding ammonium selenate or ammonium uranyl selenate to a soln. of uranyl oxide in selenic acid. The salt is soluble in water. The corresponding **potassium uranyl selenate,** $K_2(UO_2)(SeO_4)_2.2H_2O$, was prepared in a similar manner. J. Meyer and E. Kasper pointed out that with the exception of oxygen, the oxides of the elements of the sixth group combine with the oxides of elements of other groups to form heteropoly-acids. The electrolysis of these complex acids furnishes an anode liquid containing a complex uranic acid. Selenic and uranic acids thus furnish yellow **selenatouranic acid,** $H_2[UO_3(SeO_4)].2H_2O$, when a soln. of 32 grms. of uranyl nitrate and 10 grms. of selenic acid is concentrated in vacuo, and then allowed to crystallize. It is decomposed in dil., aq. soln.: $H_2[UO_3(SeO_4)].12H_2O \rightleftharpoons 3H_2O+(UO_2)SeO_4$. When a soln. containing a gram of this acid, and 1·8 grms. of potassium selenate, is boiled, **potassium hydroselenatouranate,** $KH[UO_3(SeO_4)].H_2O$, is formed; and similarly with **ammonium hydroselenatouranate,** $(NH_4)H[UO_3(SeO_4)].3H_2O$. Again, greenish-yellow **diselenatouranic acid,** $H_6[UO_3(SeO_4)_2].2H_2O$, is formed by evaporating a soln. of 32 grms. of uranyl nitrate and 15 grms. of selenic acid; while **potassium tetrahydrodiselenatouranate,** $K_2H_4[UO_4(SeO_4)_2].H_2O$, and $3H_2O$ is formed by evaporating a mixed soln. of 3·2 grms. of potassium uranate in 10 grms. of selenic acid. The ammonium and potassium complex salt prepared by R. Sendtner may belong to this series. Salts of an unknown **triselenatouranic acid,** $H_6[UO_3(SeO_4)_3]$, were obtained—**sodium dihydrotriselenatouranate,** $Na_4H_2[UO_3(SeO_4)_3].H_2O$, was obtained from a soln. of 5·5 grms. of selenatouranic acid, and 8 grms. of sodium selenate; and **sodium diammonium triselenatouranate,** $Na_4(NH_4)_2[UO_3(SeO_4)_3].10H_2O$, by the action of ammonia on the preceding salt under dry ether. A soln. of 32 grms. of uranyl nitrate and 20 grms. of selenic acid furnishes yellowish-green **triselenatouranyluranic acid,** $H_6[UO_2(UO_3)(SeO_4)_3].7H_2O$, and if a soln. is electrolyzed, crystals of the octodecahydrate collect in the anode chamber. If a soln. of 3·2 grms. of potassium uranate in 10 grms. of selenic acid be evaporated, it furnishes **potassium tetrahydrotriselenatouranyluranate,** $K_2H_4[UO_2(UO_3)(SeO_4)_3].H_2O$.

E. Mitscherlich[13] obtained **manganese selenate,** $MnSeO_4.nH_2O$, by crystallization from the aq. soln.; if at 30°–60°, rhombic plates or needles of the *dihydrate*, $MnSeO_4.2H_2O$, are formed which, according to H. Topsöe, have the axial ratios $a:b:c$=0·9959 : 1 : 0·8849, and which are isomorphous with the cadmium salt. V. Lenher and C. H. Kao obtained a soln. of the salt by the action of the acid on the carbonate. E. Mitscherlich found that the crystals are soluble in water, and their sp. gr. is 2·949; O. Pettersson gave 3·006. If the soln. be crystallized at 5° (E. Mitscherlich), or at ordinary temp. (H. Topsöe), the *pentahydrate*, $MnSeO_4.5H_2O$, is formed in pale red crystals isomorphous with the sulphate. H. Topsöe gave for the axial ratios of the triclinic crystals $a:b:c$=0·5552 : 1 : 0·5393, and α=113° 11′, β=109° 35′, and γ=92° 58′. No marked cleavage was observed. The sp. gr. is 2·334; O. Pettersson gave 2·388. H. Topsöe added that the salt is freely soluble in water; and that the aq. soln. on standing, or when warmed, deposits some manganese hydroxide. C. Schaefer and M. Schubert studied the ultra-red reflection spectrum. H. Topsöe found that when a mixed soln. of ammonium and manganese selenates is allowed to crystallize, **ammonium manganous selenate,** $(NH_4)_2Mn(SeO_4)_2.6H_2O$, is formed in pale red crystals isomorphous with the sulphate. The holohedral, prismatic, monoclinic prisms have the axial ratios $a:b:c$=0·7416 : 1 : 1·4979, and β=106° 14′; A. E. H. Tutton gave 0·7427 : 1 : 0·4979, and β=106° 16′; the topic axial ratios are $\chi:\psi:\omega$=6·3577 : 8·5302 : 4·2750. The $(\bar{2}01)$- and (010)-cleavages are marked. The optic axial angles are:

	Li-line.	*C*-line.	Na-line.	Tl-line.	Cd-line.	*F*-line.
$2E$.	120° 42′	120° 47′	121° 50′	122° 58′	123° 40′	—
$2H_a$.	63° 42′	63° 41′	63° 32′	63° 19′	63° 10′	62° 58′
$2H_o$.	97° 4′	97° 1′	96° 36′	96° 1′	95° 37′	95° 9′
$2V_a$.	70° 17′	70° 18′	70° 23′	70° 28′	70° 31′	70° 34′

The angle $2E$ decreased 6° 40′ with a rise of temp. from 15° to 75°. The sp. gr. is 2·158 at 20°/4°, and the mol. vol. 223·35. The indices of refraction are:

	Li-line.	*C*-line.	Na-line.	Tl-line.	Cd-line.	*F*-line.	*G*-line.
α . .	1·5124	1·5129	1·5160	1·5194	1·5214	1·5235	1·5394
β . .	1·5163	1·5169	1·5202	1·5237	1·5256	1·5276	1·5340
γ . .	1·5249	1·5255	1·5288	1·5323	1·5343	1·5364	1·5469

A rise of temp. of 50° diminished the refractive index about 0·0010. The sp. dispersions $\mu_G-\mu_C$ for α, β, and γ are respectively 0·0137, 0·0038, and 0·0038, and the mol. dispersions respectively 1·81, 1·87, and 1·88. The sp. refractions for the *C*-line and the μ^2-formula are 0·1393, 0·1402, and 0·1422 respectively; and the mol. refractions respectively 67·12, 67·56, and 68·51; and the mol. dispersions for the μ-formula are respectively 114·55, 115·45, and 117·37. The crystals are stable in air, and the sp. gr. is 2·093. H. Topsöe obtained **potassium manganous selenate,** $K_2Mn(SeO_4)_2.2H_2O$, in an analogous manner. The triclinic crystals have the axial ratios $a:b:c$=0·6911 : 1 : 0·4432, and α=86° 30′, β=84° 34′, and γ=101° 58′, and they are isomorphous with the corresponding sulphate. G. N. Wyrouboff also examined the crystals. H. Topsöe added that the sp. gr. is 3·070. The salt is stable in air; freely soluble in water, and when the soln. is heated, brown manganese hydroxide separates out. C. Schaefer and M. Schubert studied the ultra-red reflection spectrum. Neither A. E. H. Tutton, nor H. Topsöe succeeded in preparing the *hexahydrate*, $K_2Mn(SeO_4)_2.6H_2O$, nor has the hexahydrated potassium manganous sulphate been prepared; but the hexahydrated **rubidium manganous selenate,** $Rb_2Mn(SeO_4)_2.6H_2O$, was obtained by A. E. H. Tutton from a soln. of the component salts in equimolar proportions. The pink, holohedral, prismatic, monoclinic crystals have the axial ratios $a:b:c$=0·7422 : 1 : 0·5008, and β=105° 9′; the topic axial ratios are $\chi:\psi:\omega$=6·3333 : 8·5332 : 4·2734; the $(\bar{2}01)$-cleavage is good. The optic axial angles are:

	Li-line.	*C*-line.	Na-line.	Tl-line.	Cd-line.	*F*-line.
$2E$.	112° 11′	112° 12′	112° 24′	112° 24′	112° 45′	—
$2H_a$.	59° 36′	59° 33′	59° 21′	59° 3′	58° 51′	58° 36′
$2H_o$.	99° 40′	99° 39′	99° 16′	98° 47′	98° 28′	98° 9′
$2V_a$.	66° 5′	66° 5′	66° 2′	66° 0′	65° 57′	65° 52′

A rise of temp. from 15° to 75° decreases the optic-axial angle $2E$ by 3° 30′. The sp. gr. is 2·763 at 20°/4°, and the mol. vol. is 222·92. The indices of refraction are:

	Li-line.	*C*-line.	Na-line.	Tl-line.	Cd-line.	*F*-line.	*G*-line.
α . .	1·5059	1·5064	1·5094	1·5125	1·5163	1·5163	1·5225
β . .	1·5105	1·5110	1·5140	1·5172	1·5190	1·5210	1·5270
γ . .	1·5220	1·5226	1·5258	1·5292	1·5312	1·5332	1·5396

A rise of 50° in temp. produces a lowering of the refractive index of 0·0013. The sp. dispersions for α, β, and γ are respectively $\mu_G-\mu_C$=0·0029, 0·0029, and 0·0030; and the mol. dispersions are respectively 1·77, 1·78, and 1·84. The sp. refractions for the *C*-line and the μ^2-formula are respectively 0·1076, 0·1084, and 0·1103; the mol. refractions, respectively 66·27, 66·78, and 68·06, and the mol. refractions with the μ-formula, respectively 112·88, 113·91, and 116·50. A. E. H. Tutton prepared similar monoclinic crystals of **cæsium manganous selenate,** $Cs_2Mn(SeO_4)_2.6H_2O$, with the axial ratios $a:b:c$=0·7319 : 1 : 0·4937, and β=106° 22′; the topic axial ratios are $\chi:\psi:\omega$=6·4297 : 8·7850 : 4·3547. The $(\bar{2}01)$-cleavage is perfect. The optic axial angles are:

	Li-line.	*C*-line.	Na-line.	Tl-line.	Cd-line.	*F*-line.
$2E$.	120° 54′	120° 50′	120° 22′	120° 5′	119° 44′	—
$2H_a$.	62° 59′	62° 54′	62° 33′	61° 59′	61° 35′	61° 13′
$2H_o$.	98° 50′	98° 43′	98° 27′	98° 10′	98° 2′	97° 49′
$2V_a$.	69° 3′	69° 1′	68° 49′	68° 33′	68° 17′	68° 5′

A rise of 55° decreases the optic axial angle $2E$ by 5°. The sp. gr. is 3·008 at 20°/4°; and the mol. vol. is 235·01. The indices of refraction are:

	Li-line.	C-line.	Na-line.	Tl-line.	Cd-line.	*F*-line.	*G*-line.
α . .	1·5215	1·5220	1·5250	1·5283	1·5302	1·5323	1·5379
β . .	1·5243	1·5248	1·5279	1·5312	1·5331	1·5350	1·5605
γ . .	1·5301	1·5306	1·5338	1·5373	1·5394	1·5415	1·5474

A rise of 50° in temp. decreases the index of refraction about 0·0011. The sp. dispersions $\mu_G-\mu_C$, for α, β, and γ are respectively 0·0026, and the mol. dispersions respectively 1·83, 1·80, and 1·89. The sp. refractions for the *C*-line and the μ^2-formula are respectively 0·1014, 0·1018, and 0·1028, while the mol. refractions are respectively 71·98, 72·30, and 72·97; and the mol. refractions for the μ-formula are 123·20, 123·86, and 125·23. L. C. Lindsley and L. M. Dennis prepared **thallous manganous selenate,** $Tl_2Mn(SeO_4)_2.6H_2O$, isomorphous with the corresponding thallous salts of copper, magnesium, cobalt, and nickel. A. E. H. Tutton gave $a:b:c$=0·7463 : 1 : 0·4993, and β=105° 29′ for the axial ratios of the monoclinic crystals; the topic axial ratios are $\chi:\psi:\omega$=6·3584 : 8·5200 : 4·2540. The sp. gr.

is 3·833 at 20°/4°, and the mol. vol. 222·10. The optic axial angle $2V_a$, and the indices of refraction are:

	Li-	*C*-	Na-	Tl-	Cd-	*F*-light.
$2V_a$.	72° 1′	72° 4′	72° 27′	72° 53′	73° 10′	73° 32′
α . .	1·6213	1·6219	1·6276	1·6343	1·6379	1·6422
β . .	1·6364	1·6370	1·6429	1·6496	1·6534	1·6579
γ . .	1·6464	1·6470	1·6531	1·6598	1·6640	1·6685

The formula for β is $1{\cdot}6147+914363\lambda^{-2}+2723900000000\lambda^{-4}+\ .\ .\ .$; for α, 1·6147 is diminished by 0·0153; and for γ, raised by 0·0102. The mol. refractions by the μ-formula, for α, β, and γ, are respectively 138·12, 141·48, and 143·70; the sp. refractions by the μ^2-formula respectively 0·0919, 0·0936, and 0·0948, and the mol. refractions, respectively 78·21, 79·72, and 80·71. A. Mailhe reported the formation of **potassium manganic tetraselenate,** $K_2SeO_4.Mn_2(SeO_4)_3.24H_2O$, *potassium manganic selenium alum,* in octahedral crystals.

H. Topsöe said that iron is only slowly attacked by selenic acid at ordinary temp., but when warm, selenium separates and hydrogen selenide is evolved—*vide supra,* selenic acid. E. Wohlwill prepared **ferrous selenate,** $FeSeO_4.nH_2O$, from selenic acid and iron wire; if the soln. is evaporated in an atm. of hydrogen or carbon dioxide, and allowed to crystallize while hot, the *pentahydrate,* $FeSeO_4.5H_2O$, is formed in crystals resembling those of copper sulphate. This salt is also formed when the heptahydrate effloresces in air. If the soln. be allowed to crystallize at a low temp., near 0°, crystals of the *heptahydrate,* $FeSeO_4.7H_2O$, isomorphous with the sulphate, are formed. H. Topsöe also obtained this salt in pale, green, monoclinic crystals, from a soln. of ferrous carbonate in selenic acid. A. E. H. Tutton found that the reaction with ferrous carbonate—chalybite—and selenic acid occurs too slowly, and he obtained the soln. by the action of ferrous sulphide on a conc. soln. of selenic acid. The hydrogen sulphide liberated in the primary reaction reduces the selenic acid to some extent in accordance with the equation $3H_2S+H_2SeO_4=Se+3S+4H_2O$, but this does not interfere with the application of the method. If the filtered soln. is allowed to crystallize, monoclinic crystals of $FeSeO_4.7H_2O$ isomorphous with $FeSO_4.7H_2O$ are obtained. The crystals of the selenate are much less stable than those of ferrous sulphate, and become opaque with such rapidity that it has not been possible to make any accurate goniometric observations with them. The crystals were also examined by G. N. Wyrouboff. W. Manchot and E. Linckh studied the combinations with nitric oxide—**ferrous nitrosylselenate,** $FeSeO_4.NO$—*vide* nitric oxide, **8.** 49, 35. H. Topsöe obtained **ammonium ferrous selenate,** $(NH_4)_2Fe(SeO_4)_2.6H_2O$, by evaporating at ordinary temp. a mixed soln. of the component salts. The pale green, monoclinic crystals have the axial ratios $a:b:c=0{\cdot}7405:1:0{\cdot}5012$, and $\beta=73°\ 47'$. A. E. H. Tutton gave 0·7433 : 1 : 0·5209, and $\beta=106°\ 9'$; and for the axial ratios $\chi:\psi:\omega=6{\cdot}3212:8{\cdot}5043:4{\cdot}2684$. The $(\bar{2}01)$-cleavage is good; the (010)-cleavage is not shown. The optic axial angles are:

	Li-line.	*C*-line.	Na-line.	Tl-line.	Cd-line.	*F*-line.
$2E$.	145° 41′	146° 1′	148° 35′	149° 24′	150° 31′	151° 20′
$2H_a$.	70° 31′	70° 26′	70° 18′	70° 5′	69° 56′	69° 48′
$2H_o$.	91° 45′	91° 42′	91° 11′	90° 38′	90° 22′	90° 8′
$2V_a$.	77° 36′	77° 37′	77° 46′	77° 50′	77° 52′	77° 54′

The angle $2E$ decreases by 11° 24′ when the crystals are heated to about 60°. H. Topsöe and C. Christiansen gave $2E=142°\ 50'$, and $2V_a=76°\ 48'$. H. Topsöe gave 2·160 for the sp. gr., used for the mol. vol. 225·4. A. E. H. Tutton gave 2·191 for the sp. gr. at 20°/4°, and 220·39 for the mol. vol. The indices of refraction are:

	Li-line.	*C*-line.	Na-line.	Tl-line.	Cd-line.	*F*-line.	*G*-line.
α . . .	1·5177	1·5182	1·5216	1·5251	1·5271	1·5291	1·9356
β . . .	1·5241	1·5246	1·5280	1·5314	1·5334	1·5354	1·5422
γ . . .	1·5343	1·5348	1·5381	1·5416	1·5437	1·5457	1·5524

With a rise of temp. of about 50°, α decreases by 0·0013; β by 0·0016; and γ by 0·0018. The sp. dispersions, $\mu_G-\mu_C$, for α, β, and γ are respectively 0·0038, 0·0039, and 0·0039; and the mol. dispersions, respectively, 1·87, 1·88, and 1·87. The sp. refractions for the *C*-line and the μ^2-formula are respectively 0·1384, 0·1398, and 0·1420; and the mol. refractions, 66·81, 67·50, and 68·59. The mol. refractions for the μ-formula are respectively 114·21, 115·62, and 117·87. According to H. Topsöe, the dry salt is fairly stable in air, but the aq. soln. decomposes rapidly when warmed, depositing a basic salt. Similarly with **potassium ferrous selenate,** $K_2Fe(SeO_4)_2.6H_2O$, which furnishes pale green, monoclinic plates of the *hexahydrate,* with the axial ratios $a:b:c=0·7407:1:0·5507$, and $\beta=75° 45'$. A. E. H. Tutton gave 0·7490 : 1 : 0·5044, and $\beta=105° 50'$; and for the topic axial ratios $\chi:\psi:\omega=6·2230:8·3083:4·1908$. The (201)-cleavage is shown by the crystals. The optic axial angles are:

	Li-line.	*C*-line.	Na-line.	Tl-line.	Cd-line.	*F*-line.
$2V_o$.	116° 49′	116° 48′	116° 42′	116° 35′	116° 30′	116° 24′
$2H_a$.	63° 11′	64° 12′	64° 18′	64° 25′	64° 30′	64° 36′

The sp. gr. is 2·494 at 20°/4°, and the mol. vol. 210·39. The indices of refraction are:

	Li-line.	*C*-line.	Na-line.	Tl-line.	Cd-line.	*F*-line.	*G*-line.
α . . .	1·5059	1·5064	1·5095	1·5127	1·5145	1·5194	1·5224
β . . .	1·5144	1·5149	1·5182	1·5225	1·5215	1·5253	1·5314
γ . . .	1·5306	1·5311	1·5245	1·5379	1·5399	1·5421	1·5483

The sp. dispersions, $\mu_G-\mu_C$, for α, β, and γ are respectively 0·0032, 0·0032, and 0·0033, and the mol. dispersions 1·64, 1·70, and 1·75. The sp. refractions for the *C*-line, and the μ^2-formula are 0·1192, 0·1209, and 0·1241 respectively; and the mol. refractions respectively 62·55, 63·43, and 65·10. The mol. refractions by the μ-formula are respectively 106·54, 108·33, and 111·74. H. Topsöe found that the aq. soln. decomposes as in the case of the ammonium salt. Hot aq. soln. also deposit triclinic crystals of the *dihydrate,* isomorphous with the manganese salt. According to A. E. H. Tutton, the dihydrate is formed in monoclinic crystals if the soln. be evaporated at ordinary temp., and the hexahydrate when the temp. is near 0°.

A. E. H. Tutton found that **rubidium ferrous selenate,** $Rb_2Fe(SeO_4)_2.6H_2O$, furnishes pale bluish-green, holohedral, prismatic, monoclinic crystals with the axial ratios $a:b:c=0·7424:1:0·5000$, and $\beta=104° 57'$, and the topic axial ratios $\chi:\psi:\omega=6·3109:8·5006:6·2503$. The $(\bar{2}01)$-cleavage is good. The optic axial angles are:

	Li-line.	*C*-line.	Na-line.	Tl-line.	Cd-line.	*F*-line.
$2E$.	130° 27′	130° 32′	131° 5′	131° 38′	132° 0′	132° 33′
$2H_a$.	66° 36′	66° 4′	66° 17′	65° 39′	65° 47′	65° 33′
$2H_o$.	94° 30′	94° 26′	94° 5′	93° 39′	93° 22′	93° 6′
$2V_a$.	73° 35′	73° 34′	73° 32′	73° 30′	73° 28′	73° 26′

A rise of 70° in temp. increases the angle $2E$ by 2°. The sp. gr. is 2·800 at 20°/4°, and the mol. vol. 220·29. The indices of refraction are:

	Li-line.	*C*-line.	Na-line.	Tl-line.	Cd-line.	*F*-line.	*G*-line.
α . . .	1·5099	1·5104	1·5133	1·5165	1·5184	1·5202	1·5264
β . . .	1·5165	1·5170	1·5200	1·5233	1·5252	1·5272	1·5334
γ . . .	1·5290	1·5295	1·5328	1·5363	1·5382	1·5404	1·5467

A rise of temp. of 50° decreases α by 0·0016, β by 0·0018, and γ by 0·0021. The sp. dispersions, $\mu_G-\mu_C$, for α, β, and γ are 0·0028, 0·0029, and 0·0030 respectively; and the mol. dispersions, 1·73, 1·76, and 1·83 respectively. The sp. refractions for the *C*-line and the μ^2-formula are respectively 0·1069, 0·1080, and 0·1102; and the mol. refractions 65·93, 66·65, and 68·00 respectively. The mol. refractions for the μ-formula are 112·44, 113·89, and 116·65 respectively. A. E. H. Tutton prepared **cæsium ferrous selenate,** $Cs_2Fe(SeO_4).6H_2O$, in bluish-grey, holohedral, prismatic, monoclinic crystals with the axial ratios $a:b:c=0·7308:1:0·4979$, and $\beta=106° 2'$; and the topic axial ratios $\chi:\psi:\omega=6·3847:8·7366:4·3499$. The ($\bar{2}01$)-cleavage is excellent. The optic axial angle $2E$ in air is too large for measurement; the other angles are:

	Li-line.	*C*-line.	Na-line.	Tl-line.	Cd-line.	*F*-line.
$2H_a$.	75° 28′	75° 23′	75° 0′	74° 26′	74° 7′	73° 53′
$2H_o$.	87° 33′	87° 27′	87° 22′	87° 6′	87° 58′	86° 49′
$2V_a$.	82° 58′	82° 56′	82° 47′	82° 33′	82° 25′	82° 20′

The sp. gr. is 3·048 at 20°/4°, and the mol. vol. 233·21. The indices of refraction are:

	Li-line.	*C*-line.	Na-line.	Tl-line.	Cd-line.	*F*-line.	*G*-line.
α . .	1·5269	1·5274	1·5306	1·5339	1·5359	1·5379	1·5442
β . .	1·5317	1·5322	1·5352	1·5385	1·5405	1·5425	1·5488
γ . .	1·5379	1·5384	1·5414	1·5450	1·5470	1·5491	1·5555

The sp. dispersions, $\mu_G-\mu_C$, for α, β, and γ are 0·0027, 0·0026, and 0·0027 respectively; and the mol. dispersions, respectively 1·90, 1·87, and 1·92. The mol. refractions for the *C*-line and the μ^2-formula are respectively 0·1009, 0·1017, and 0·1027, and the mol. refractions respectively 71·74, 72·29, and 72·99. The mol. refractions for the μ-formula are respectively 122·99, 124·11, and 125·56. A. E. H. Tutton found that the monoclinic crystals of **thallous ferrous selenate,** $Tl_2Fe(SeO_4)_2.6H_2O$, have the axial ratios $a:b:c=0·7445:1:0·5011$, and $\beta=105° 27'$; the topic axial ratios are $\chi:\psi:\omega=6·2846:8·4415:4·2300$. The sp. gr. is 3·940 at 20°/4°, and the mol. vol. 216·30. The optic axial angles, and the indices of refraction, are:

	Li-	*C*-	Na-	Tl-	Cd-	*F*-light.
$2V_a$.	69° 1′	69° 5′	69° 36′	70° 3′	70° 20′	70° 45′
$2E$.	125° 25′	125° 48′	130° 6′	134° 18′	135° 48′	140° 30′
α .	1·6291	1·6297	1·6352	1·6415	1·6452	1·6496
β .	1·6453	1·6459	1·6514	1·6578	1·6617	1·6662
γ .	1·6527	1·6533	1·6589	1·6655	1·6695	1·6743

The formula for β is $1·6265+745318\lambda^{-2}+4616300000000\lambda^{-4}+\ldots$; for α, 1·6265 is decreased by 0·0162, and for γ, raised by 0·0075. The mol. refractions by the μ-formula for α, β, and γ are respectively 136·20, 139·71, and 141·31; the sp. refractions by the μ^2-formula are respectively 0·0903, 0·0921, and 0·0929, and the mol. refractions respectively 76·93, 78·50, and 79·21.

C. Roncagliolo prepared **rubidium ferric selenate,** $Rb_2SeO_4.Fe_2(SeO_4)_3.24H_2O$, or *rubidium selenatoferrate*, $RbFe(SeO_4)_2.12H_2O$, by dissolving freshly precipitated ferric hydroxide in an excess of selenic acid, and adding the calculated amount of rubidium carbonate. The soln. deposits the salt in pale violet crystals belonging to the cubic system. The sp. gr. of the salt is 2·1305 at 18°; and at 40°–45° it melts in its water of crystallization to form a red liquid: the index of refraction is 1·50473 for the medium red line; 1·50699 for the *D*-line; 1·51190 for the medium green line; 1·51725 for the medium blue line; and 1·52290 for the medium violet line. Under analogous circumstances, **cæsium ferric selenate,** $Cs_2SeO_4.Fe_2(SeO_4)_3.24H_2O$, or *cæsium selenatoferrate*, $CsFe(SeO_4)_3.12H_2O$, is formed in violet crystals belonging to the cubic system. The sp. gr. of the salt is 3·6176 at 15°; and at 55°–60° it melts in its water of crystallization. The index of refraction is 1·50884 for the medium red line; 1·51164 for the *D*-line; 1·51615 for the medium green line; 1·52092 for the medium blue line; and 1·52645 for the medium violet line. If in the preparation of this alum, the soln. be heated excessively, a greenish-yellow, basic alum is deposited.

H. Copaux[14] obtained an unstable crystalline magma of **cobaltic selenate,** $Co_2(SeO_4)_3.18H_2O$, by electrolyzing a soln. of cobaltous selenate in 40 per cent. selenic acid at —10°. A soln. of cobaltous hydroxide or carbonate furnishes a soln. of **cobaltous selenate,** which, when evaporated between 30° and 40°, furnished E. Mitscherlich with triclinic crystals of the *pentahydrate*, $CoSeO_4.5H_2O$, isomorphous with the corresponding manganese sulphate. V. Lenher and C. H. Kao obtained a soln. of the salt by the action of the acid on the carbonate. G. N. Wyrouboff obtained ruby-red, triclinic crystals of this salt by evaporating the soln. at 50°–60°. The crystals were examined by G. N. Wyrouboff, and H. Topsöe. The latter found the crystals to be stable in air; to have a sp. gr. of 2·512; to be freely soluble in water; and to effloresce superficially in air at a temp. exceeding 50°. E. Mitscherlich said that if the aq. soln. be evaporated over 15°, monoclinic crystals of the *hexahydrate*, $CoSeO_4.6H_2O$, are formed isomorphous with the corresponding sulphate. The monoclinic prisms were found by H. Topsöe to have the axial ratios $a:b:c=1·5709:1:1·6815$, and $\beta=98° 14'$. G. N. Wyrouboff also made some observations on the crystals. The $(10\bar{1})$-cleavage is complete. The optical character is negative. E. Herlinger studied the structure of the crystals. H. Topsöe and C. Christiansen gave for the optic axial angle for Na-light, $2V=7° 13'$, and $2E=11° 0'$, and the indices of refraction $\beta=1·5225$, and $\gamma=1·5227$, while for Li-light, $\beta=1·5183$. H. Topsöe gave 2·175 for the sp. gr.; and G. Woulff, 2·32. The crystals are stable in air, and freely soluble in water. If the aq. soln. be evaporated below 10°, E. Mitscherlich found that crystals of the *heptahydrate*, $CoSeO_4.7H_2O$, are produced; H. Topsöe obtained monoclinic prisms by evaporating the soln. at 5°–6°. The axial ratios are $a:b:c=1·1833:1:1·545$, and $\beta=104° 57'$. G. N. Wyrouboff also examined the crystals. H. Topsöe found the sp. gr. to be 2·135; and J. A. Groshans compared the sp. gr. of the sulphates and selenates. H. Topsöe said that the crystals readily pass into the hexahydrate when exposed to air. According to P. Bogdan, if an aq. soln. of the normal selenate be heated for 10–12 hrs. in a sealed tube at 100°, a red mass of **cobalt dihydroxytriselenate**, $Co(OH)_2.3CoSeO_4$, is formed. It is insoluble in water; soluble in acids; loses no water at 210°; and decomposes at 250°.

C. von Hauer, and H. Topsöe prepared **ammonium cobaltous selenate**, $(NH_4)_2Co(SeO_4)_2.6H_2O$, by evaporating a soln. of the component salts. The ruby-red crystals are isomorphous with the corresponding sulphate; and H. Topsöe gave for the axial ratios of the monoclinic prisms, $a:b:c=0·7414:1:0·5037$, and $\beta=106° 23'$. A. E. H. Tutton gave 0·7449 : 1 : 0·5031, and $\beta=106° 53'$; the topic axial ratios are 6·3057 : 8·4651 : 4·2587. The $(\bar{2}01)$-cleavage is perfect, and the (010)-cleavage is less clear. The optic axial angle $2E$ in air is so large as to be indeterminable, while for

	Li-line.	*C*-line.	Na-line.	Tl-line.	Cd-line.
$2H_a$.	74° 39′	74° 38′	74° 28′	74° 15′	74° 5′
$2H_o$.	88° 18′	88° 14′	87° 46′	87° 16′	86° 50′
$2V_a$.	82° 5′	82° 6′	82° 14′	82° 22′	82° 28′

H. Topsöe and C. Christiansen gave $2V_a=82° 1'$ for the Na-light. H. Topsöe gave for the sp. gr. 2·212. A. E. H. Tutton gave 2·228 at 20°/4°, and 218·10 for the mol. vol. J. A. Groshans made a comparative study of the sp. gr. of the sulphates and selenates. H. Topsöe and C. Christiansen found that the optical character is negative; and the indices of refraction for Na-light, $\alpha=1·5246$, $\beta=1·5311$, and $\gamma=1·5396$; while for the *C*-line, $\beta=1·5280$; for the *F*-line, 1·5392; and for the *G*-line, 1·5455. C. Schaefer and M. Schubert studied the ultra-red reflection spectrum. A. E. H. Tutton gave for the indices of refraction:

	Li-line.	*C*-line.	Na-line.	Tl-line.	Cd-line.	*F*-line.	*G*-line.
α . .	1·5223	1·5228	1·5261	1·5294	1·5315	1·5335	1·5398
β . .	1·5287	1·5292	1·5327	1·5362	1·5380	1·5401	1·5466
γ . .	1·5377	1·5388	1·5417	1·5453	1·5474	1·5496	1·5562

There is an increase of about 0·0013 for a rise of temp. of 60°. The sp. dispersions for α, β, and γ are respectively $\mu_G-\mu_C=0·0037$, 0·0038, and 0·0039; and the mol. dispersions 1·71, 1·84, and 1·89. The sp. refractions for *C*-line and the μ^2-formula are respectively 0·1371, 0·1385, and 0·1404; and the mol. refractions are respectively 114·02, 115·42, and 117·38. J. Ferguson found for the equilibrium press. in the system $(NH_4)_2Co(SeO_4)_2.6H_2O \rightleftharpoons (NH_4)_2Co(SeO_4)_2.2H_2O + 4H_2O$:

	27·0°	34·1°	41·5°	56·3°	45·6°	68·4°	71·1°
Press. .	3·4	5·9	10·3	29·5	53·1	64·8	75·5 mm.

H. Topsöe found that the salt is stable in air; and freely soluble in water.

C. von Hauer, and H. Topsöe prepared **potassium cobaltous selenate,** $K_2Co(SeO_4)_2.6H_2O$, in a similar manner. The crystals are isomorphous with the corresponding sulphate. The garnet-red, monoclinic crystals were found by H. Topsöe to have the axial ratios $a : b : c = 0·7379 : 1 : 0·5856$, and $\beta = 104° 10'$. A. E. H. Tutton gave 0·7522 : 1 : 0·5062, and $\beta = 104° 17'$; and for the topic axial ratios $\chi : \psi : \omega = 6·2197 : 8·2688 : 4·1856$. The $(\bar{2}01)$-cleavage is excellent. The optic axial angles are:

	Li-line.	*C*-line.	Na-line.	Tl-line.	Cd-line.
$2E$.	103° 43′	103° 49′	104° 25′	105° 18′	105° 46′
$2H_a$.	56° 37′	56° 37′	56° 33′	56° 28′	—
$2H_o$.	103° 38′	103° 36′	103° 9′	102° 35′	—
$2V_a$.	62° 12′	62° 13′	62° 19′	62° 27′	—

The angle $2E$ increases about 5° 30′ when heated from ordinary temp. to 80°. The sp. gr. is 2·514. A. E. H. Tutton gave 2·530 at 20°/4°, and for the mol. vol., 208·60. J. A. Groshans made a comparative study of the sp. gr. of these salts. H. Topsöe and C. Christiansen found the optical character to be positive and the indices of refraction for the Na-light, $\alpha = 1·5035$, $\beta = 1·5195$, and $\gamma = 1·5358$; and $\beta = 1·5162$ for *C*-light, and 1·5270 for *F*-light. A. E. H. Tutton gave for the indices of refraction:

	Li-line.	*C*-line.	Na-line.	Tl-line.	Cd-line.	*F*-line.	*G*-line.
α . .	1·5122	1·5127	1·5158	1·5191	1·5211	1·5231	1·5393
β . .	1·5181	1·5186	1·5218	1·5250	1·5271	1·5291	1·5354
γ . .	1·5341	1·5347	1·5380	1·5415	1·5435	1·5456	1·5522

A rise of temp. of 60° decreases the refractive indices by about 0·0026. The sp. dispersions for α, β, and γ are respectively $\mu_G - \mu_C = 0·0033$, 0·0032, and 0·0033; and the mol. dispersions respectively 1·70, 1·71, and 1·77. The sp. refractions for the *C*-line and the μ^2-formula are respectively 0·1187, 0·1199, and 0·1230; and the mol. refractions respectively 62·66, 63·27, and 64·91. The mol. refractions by the μ-formula are respectively 186·99, 109·18, and 111·54. The crystals are stable in air. J. Ferguson found for the equilibrium press. in the system $K_2Co(SeO_4)_2.6H_2O \rightleftharpoons K_2Co(SeO_4)_2.2H_2O + 4H_2O$:

	26·1°	33·0°	42·5°	43·8°	48·5°	61·2°	68·2°
Press. .	21·4	33·5	58·5	62·4	79·9	148·5	199·2 mm.

L. C. Lindsley and L. M. Dennis prepared **thallous cobaltous selenate,** $Tl_2Co(SeO_4)_2.6H_2O$, isomorphous with the corresponding thallous salts of copper, nickel, magnesium, and manganese. A. E. H. Tutton gave for the axial ratios of the monoclinic crystals $a : b : c = 0·7463 : 1 : 0·5021$, and $\beta = 105° 40'$; the topic axial ratios are $\chi : \psi : \omega = 6·2696 : 8·4010 : 4·2181$; the sp. gr., 3·998 at 20°/4°; and the mol. vol., 213·92. The optic axial angles, and the indices of refraction are:

	Li-	*C*-	Na-	Tl-	Cd-	*F*-light.
$2V_a$.	66° 11′	66° 15′	66° 42′	67° 4′	67° 18′	67° 36′
$2E$.	111° 4′	111° 10′	112° 30′	113° 40′	114° 25′	115° 10′
α .	1·6397	1·6402	1·6442	1·6485	1·6515	1·6552
β .	1·6490	1·6495	1·6535	1·6578	1·6608	1·6646
γ .	1·6545	1·6550	1·6590	1·6635	1·6666	1·6706

The formula for β is $1·6322 + 798284\lambda^{-2} + 1561300000000\lambda^{-4} + \ldots$; for α, 1·6322 is diminished by 0·0093, and for γ, increased by 0·0056. The mol. refractions by the μ-formula for α, β, and γ, are respectively 136·96, 138·94, and 140·12; the sp.

refractions by the μ^2-formula are respectively 0·0901, 0·0911, and 0·0918; and the mol. refractions, respectively 77·09, 77·96, and 78·50.

A. E. H. Tutton prepared **rubidium cobalt selenate,** $Rb_2Co(SeO_4)_2.6H_2O$, in ruby-red, holohedral, monoclinic prisms showing more or less tabular forms, and with the axial ratios $a:b:c=0·7427:1:0·5019$, and $\beta=105° 14'$; and the topic axial ratios $\chi:\psi:\omega=6·2901:8·4693:4·2508$. The cleavage parallel to $(\bar{2}01)$ is perfect. The optic axial angles are:

	Li-line.	*C*-line.	Na-line.	Tl-line.
$2E$.	131° 8′	131° 14′	132° 5′	133° 0′
$2H_a$.	66° 50′	66° 47′	66° 28′	66° 9′
$2H_o$.	94° 35′	94° 31′	94° 9′	93° 45′

The optic axial angle $2E$ increases about 5° for a rise of temp. of about 65°. The sp. gr. is 2·837 at 20°/4°, and the mol. vol. 218·49. The indices of refraction are:

	Li-line.	*C*-line.	Na-line.	Tl-line.	Cd-line.	*F*-line.	*G*-line.
α . .	1·5163	1·5168	1·5199	1·5232	1·5252	1·5273	1·5333
β . .	1·5220	1·5225	1·5256	1·5290	1·5311	1·5332	1·5393
γ . .	1·5329	1·5334	1·5369	1·5404	1·5425	1·5446	1·5508

There is a decrease of about 0·0025 for 60° rise of temp. The sp. dispersions for α, β, and γ are 0·0028, 0·0029, and 0·0029 respectively; and the mol. dispersions are 1·76, 1·79, and 1·83 respectively. The sp. refractions for the *C*-line and the μ^2-formula are 0·1066, 0·1076, and 0·1095; and the mol. refractions are 66·08, 66·69, and 67·86 respectively. The mol. refractions with the μ-formula are respectively 112·92, 114·16, and 116·54.

A. E. H. Tutton likewise prepared **cæsium cobaltous selenate,** $Cs_2Co(SeO_4)_2.6H_2O$, in red, holohedral, monoclinic prisms with the axial ratios $a:b:c=0·7310:1:0·4989$, and $\beta=106° 18'$. The topic axial ratios are $\chi:\psi:\omega=6·3618:8·7028:4·3418$. The $(\bar{2}01)$-cleavage is perfect. The optic axial angle $2E$ is so large that it does not emerge in air:

	Li-line.	*C*-line.	Na-line.	Tl-line.
$2H_a$.	79° 23′	79° 17′	78° 41′	78° 9′
$2H_o$.	84° 17′	84° 16′	84° 11′	84° 3′
$2V_a$.	87° 11′	87° 8′	86° 48′	86° 32′

The sp. gr. is 3·094 at 20°/4°, and the mol. vol. 230·73. The indices of refraction are:

	Li-line.	*C*-line.	Na-line.	Tl-line.	Cd-line.	*F*-line.	*G*-line.
α . .	1·5316	1·5321	1·5354	1·5389	1·5409	1·5430	1·5492
β . .	1·5360	1·5365	1·5399	1·5434	1·5454	1·5475	1·5539
γ . .	1·5412	1·5418	1·5453	1·5489	1·5510	1·5531	1·5596

The refractive indices diminish by about 0·0018 for 60° rise of temp. The sp. dispersion, $\mu_G-\mu_C$, for α, β, and γ are respectively 0·0026, 0·0027, and 0·0027; and the mol. dispersions 1·90, 1·93, and 1·97. The sp. refractions for the *C*-line and the μ^2-formula are respectively 0·1002, 0·1009, and 0·1017, and the mol. refractions respectively 171·51, 72·00, and 72·59; while for the μ-formula, the mol. refractions are respectively 122·77, 123·79, and 125·01.

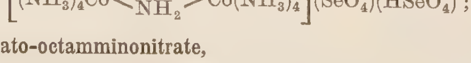
C. T. Klobb prepared **cobaltic hexamminoselenate,** $[Co(NH_3)_6]_2(SeO_4)_3.5H_2O$, by evaporating a neutral soln. of cobaltic hexamminohydroxide in selenic acid; the brownish-yellow monoclinic prisms have the axial ratios $a:b:c=1·1350:1:1·4023$, and $\beta=90° 35'$. This salt was also prepared by J. Meyer and H. Moldenhauer. C. T. Klobb prepared **cobaltic hexamminohydroselenate,** $[Co(NH_3)_6](SeO_4)(HSeO_4).2\frac{1}{2}H_2O$, from a soln. of the former salt with an excess of selenic acid. The salt is not decomposed by water. The triclinic crystals have the axial ratios $a:b:c=0·8455:1:0·4729$, and $\alpha=99° 10'$, $\beta=86° 47'$, and $\gamma=88° 50'$, and **ammonium cobaltous hexamminoselenate,** $[Co(NH_3)_6](SeO_4)(NH_4SeO_4).4H_2O$, by neutralizing the hydroselenate with ammonia. The crystals are isomorphous with the corresponding sulphate; the axial ratios of the rhombic crystals are $a:b:c=0{\cdot}9595:1:1{\cdot}2024$. In addition to the *tetrahydrate*, a *dihydrate* was also obtained in monoclinic crystals with the axial ratios $a:b:c=1{\cdot}4285:1:0{\cdot}6469$, and $\beta=94°\ 42'$. F. M. Jäger reviewed the characteristics of these salts. J. Meyer and K. Gröhler prepared **cobaltic trisethylenediaminotrihydroselenate**, $[Coen_3](HSeO_4)_3$, where "en" is written in place of $C_2H_4(NH_2)_2$; they also obtained **cobaltic trisethylenediaminohydroselenate**, $[Coen_3](SeO_4)(HSeO_4)_5$, and **cobaltic trisethylenediaminoselenate**, $[Coen_3]_2(SeO_4)_3.H_2O$.

J. Meyer and H. Moldenhauer prepared **cobaltic aquopentamminoselenate**, $[Co(H_2O)(NH_3)_5]_2(SeO_4)_3.3H_2O$, analogous to roseocobaltic sulphate; **cobaltic chloropentamminoselenate**, $[CoCl(NH_3)_5]SeO_4$, analogous to purpureocobaltic sulphate; **cobaltic nitritopentamminoselenate**, $[Co(NO_2)(NH_3)_5]SeO_4$, which like the sulphate forms a periodide; **cobaltic sulphatopentamminoselenate**, $Co(SO_4)(NH_3)_5]_2SeO_4.2H_2O$, the corresponding sulphate is monohydrated; **cobaltic selenatopentamminohydroselenate**, $[Co(SeO_4)(NH_3)_5]HSeO_4.2H_2O$, which formed the starting point for the preparation of a series of related selenatopentammines—**cobaltic selenatopentamminoselenate**, $[Co(SeO_4)(NH_3)_5]_2SeO_4.H_2O$; **cobaltic selenatopentamminosulphate**, $[Co(SeO_4)(NH_3)_5]_2SO_4.H_2O$; **cobaltic selenatopentamminonitrate**, $[Co(SeO_4)(NH_3)_5]NO_3$; **cobaltic selenatopentamminobromide**, $[Co(SeO_4)(NH_3)_5]Br$; and **cobaltic selenatopentamminochloroplatinate**, $[Co(SeO_4)(NH_3)_5]_2.PtCl_6.2H_2O$. J. N. Brönsted and A. Petersen found the molar solubility of **cobaltic dinitritotetramminoselenate**, $[Co(NH_3)_4(NO_2)_2]_2SeO_4$, to be 0·0092 at 20°. J. Meyer and co-workers also prepared **cobaltic nitratopentamminohydroselenate**, $[Co(NH_3)_5(NO_3)]HSeO_4$; as well as **cobaltic thiocarbimidopentamminoselenate**, $[Co(NH_3)_5(NCS)]_2SeO_4.2H_2O$; **cobaltic carbonatopentamminoselenate**, $[Co(NH_3)_5(CO_3)]_2SeO_4$; **cobaltic oxalatopentamminoselenate**, $[Co(NH_3)_5(C_2O_4)]_2SeO_4.3H_2O$; and **cobaltic oxalatopentamminohydroselenate**, $[Co(NH_3)_5(C_2O_4)]HSeO_4.H_2O$.

J. Meyer and H. Moldenhauer prepared **cobaltic diaquotetramminoselenate**, $[Co(H_2O)_2(NH_3)_4]_2(SeO_4)_3.3H_2O$; **cobaltic carbonatotetramminoselenate**, $[Co(CO_3)(NH_3)_4]_2SeO_4.3H_2O$; **cobaltic transdichlorotetramminohydroselenate**, $[CoCl_2(NH_3)_4]HSeO_4$; **cobaltic transdichlorotetrapyridinohydroselenate**, $[CoCl_2Py_4]HSeO_4.2H_2O$; **cobaltic cis-dinitritotetramminoselenate**, $[Co(NO_2)_2(NH_3)_4]_2SeO_4$, from flaveocobaltic nitrate; and **cobaltic transdinitritotetramminoselenate**, $[Co(NO_2)_2(NH_3)_4]_2.SeO_4$, from croceo-cobaltic chloride. J. Meyer and co-workers prepared **cobaltic aquonitratotetramminohydroselenate**, $[Co(NH_3)_4(H_2O)(NO_3)](HSeO_4)_2$; **cobaltic aquonitritotetramminoselenate**, $[Co(NH_3)_4(H_2O)(NO_2)]_2SeO_4$; **cobaltic bishydroselenatotetramminoselenate**, $[Co(NH_3)_4(HSeO_4)_2]SeO_4.4H_2O$; **cobaltic aquohydroxytetramminoselenate**, $Co(NH_3)_4(H_2O)(HO)SeO_4$; **cobaltic aquoselenatotetramminoselenate**, $[Co(NH_3)_4(H_2O)(SeO_4)]_2SeO_4$; **cobaltic aquoselenatotetramminohydroselenate**, $[Co(NH_3)_4(H_2O)(SeO_4)]HSeO_4$; **cobaltic aquoselenatotetramminochloride**, $[Co(NH_3)_4(H_2O)(SeO_4)]Cl$; **cobaltic aquoselenatotetramminosulphate**, $[Co(NH_3)_4(H_2O)(SeO_4)]_2SO_4.4H_2O$: **cobaltic aquosulphatotetramminoselenate**, $[Co(NH_3)_4(H_2O)(SO_4)]_2SeO_4.4H_2O$; **cobaltic aquochlorotetramminoselenate**, $[Co(NH_3)_4(H_2O)Cl]_2SeO_4$; **cobaltic aquobromotetramminoselenate**, $[Co(NH_3)_4(H_2O)Br]_2SeO_4$; **cobaltic oxalatotetramminoselenate**, $[Co(NH_3)_4(C_2O_4)]_2SeO_4.2H_2O$; **cobaltic oxalatodiethylenediaminoselenate**, $[Co,en_2(C_2H_2O_4)]_2SeO_4.3H_2O$; and **cobaltic dithiocarbimidobisethylenediaminohydroselenate**, $[Co,en_2(CNS)_2]_2HSeO_4$.

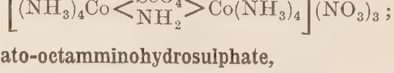
J. Meyer and co-workers prepared **cobaltic diaquochlorotriamminoselenate**, $[Co(NH_3)_3(H_2O)_2Cl]_2SeO_4$; and also **cobaltic diaquodipyridinodiamminohydroselenate**, $[Co(NH_3)_2(C_5H_5N)_2(H_2O)_2]_2SeO_4(HSeO_4)$; **cobaltic diaquodichlorodiamminohydroselenate**, $[Co(NH_3)_2(H_2O)_2Cl_2]HSeO_4$; and **cobaltic bisdimethylglyoximinodiamminoselenate**, $[Co(C_4H_7O_2N_2)_2(NH_3)_2]_2SeO_4$.

A number of other complex selenates was prepared by J. Meyer and co-workers, thus, **dicobaltic tetranitrito-μ-selenatohexammine**, $[(NH_3)_3(NO_2)_2Co.SeO_4.Co(NO_2)_2(NH_3)_3].2H_2O$; **trihydrated dicobaltic peroxydecamminoselenate**, $[(NH_3)_5Co.O_2.Co(NH_3)_5](SeO_4)_2.3H_2O$; **octohydrated dicobaltic peroxydecamminoselenate**, $[(NH_3)_5Co.O_2.Co(NH_3)_5](SeO_4)_5.8H_2O$; **dicobaltic peroxydecamminohydroselenate**, $[(NH_3)_5CoO_2Co(NH_3)_5](HSeO_4)_4$; **dicobaltic μamidodecamminoselenate**, $[(NH_3)_5Co.NH_2.Co(NH_3)_5]_2(SeO_4)_5$; **dicobaltic μamidoaquochloroctamminoselenate**, $[Cl(NH_3)_4Co.NH_2.Co(NH_3)_4(H_2O)](SeO_4)_2$; **dicobaltic μ-amido-octamminohydroselenate**,



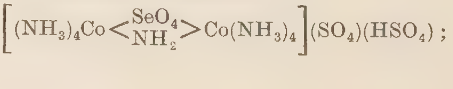
$$\left[(NH_3)_4Co{<}\begin{matrix}SeO_4\\NH_2\end{matrix}{>}Co(NH_3)_4\right](SeO_4)(HSeO_4)\ ;$$

dicobaltic μ-amidoselenato-octamminonitrate,



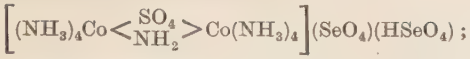
$$\left[(NH_3)_4Co{<}\begin{matrix}SeO_4\\NH_2\end{matrix}{>}Co(NH_3)_4\right](NO_3)_3\ ;$$

dicobaltic μ-amidoselenato-octamminohydrosulphate,



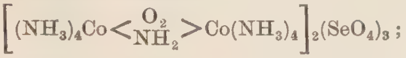
$$\left[(NH_3)_4Co{<}\begin{matrix}SeO_4\\NH_2\end{matrix}{>}Co(NH_3)_4\right](SO_4)(HSO_4)\ ;$$

dicobaltic μ-amidosulphato-octamminohydroselenate,



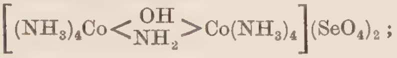
$$\left[(NH_3)_4Co<\genfrac{}{}{0pt}{}{SO_4}{NH_2}>Co(NH_3)_4\right](SeO_4)(HSeO_4) ;$$

dicobaltic μ-amidoperoxyoctamminoselenate,



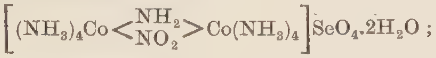
$$\left[(NH_3)_4Co<\genfrac{}{}{0pt}{}{O_2}{NH_2}>Co(NH_3)_4\right]_2(SeO_4)_3 ;$$

dicobaltic μ-amidohydroxyoctamminoselenate,



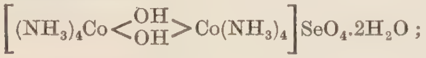
$$\left[(NH_3)_4Co<\genfrac{}{}{0pt}{}{OH}{NH_2}>Co(NH_3)_4\right](SeO_4)_2 ;$$

dicobaltic μ-amidonitrito-octamminoselenate,



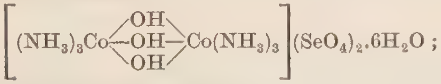
$$\left[(NH_3)_4Co<\genfrac{}{}{0pt}{}{NH_2}{NO_2}>Co(NH_3)_4\right]SeO_4.2H_2O ;$$

dicobaltic dihydroxyoctamminoselenate,

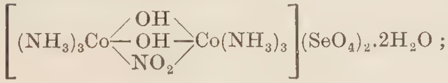


$$\left[(NH_3)_4Co<\genfrac{}{}{0pt}{}{OH}{OH}>Co(NH_3)_4\right]SeO_4.2H_2O ;$$

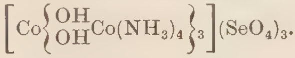
dicobaltic trihydroxyhexamminoselenate,



dicobaltic μ-nitritodihydroxyhexamminoselenate,



tetracobaltic hexahydroxydodecamminoselenate,



$$\left[Co\left\{\genfrac{}{}{0pt}{}{OH}{OH}Co(NH_3)_4\right\}_3\right](SeO_4)_3.$$

E. Mitscherlich[15] prepared **nickel selenate,** $NiSeO_4.6H_2O$, by crystallizing a soln. of the salt at ordinary temp.; and the same hydrate is produced if the temp. of crystallization ranges from 4° to 80°. It was also prepared by C. von Hauer. V. Lenher and C. H. Kao obtained a soln. of the salt by the action of the acid on the carbonate. H. Topsöe said that the tetragonal crystals have the axial ratio $a:c$=1 : 1·8364, and they are isomorphous with the corresponding sulphate, and with zinc selenate. G. N. Wyrouboff said that the salt is dimorphous like the corresponding sulphate, for he was able to obtain monoclinic as well as tetragonal crystals. The crystals are stable in air, and H. Topsöe gave 2·314 for the sp. gr. H. Topsöe and C. Christiansen gave for the indices of refraction for the *C*-, *D*-, and *F*-lines α=1·5257, 1·5393, and 1·5473 respectively; and γ=1·5089, 1·5125, and 1·5196 respectively. G. L. Clark found that the vap. press. of **nickel hexamminoselenate,** $Ni(NH_3)_6SeO_4$, at 441° is 760 mm. C. von Hauer prepared **ammonium nickel selenate,** $(NH_4)_2Ni(SeO_4)_2.6H_2O$, from a soln. of the component salts. H. Topsöe said that the emerald green crystals are isomorphous with the corresponding sulphate; the axial ratios of the monoclinic crystals are 0·7378 : 1 : 0·5042, and β=106° 19′. A. E. H. Tutton gave 0·7395 : 1 : 0·5048, and β=106° 17′. The topic axial ratios are $\chi:\psi:\omega$=6·2520 : 8·4543 : 4·2678 ; the $(\bar{2}01)$-cleavage is well-developed, and the (010)-cleavage is not so distinct. The optic axial angle $2E$ is too large for measurement, while

	Li-line.	*C*-line.	Na-line.	Tl-line.	Cd-line.	*F*-line.
$2H_a$.	78° 43′	78° 41′	78° 12′	78° 4′	77° 53′	77° 41′
$2H_o$.	85° 5′	85° 3′	84° 40′	84° 15′	83° 58′	83° 39′
$2V_a$.	86° 19′	86° 19′	86° 21′	86° 24′	86° 26′	86° 29′

H. Topsöe and C. Christiansen gave $2V_a$=86° 14′. H. Topsöe found the sp. gr. to be 2·212, and J. A. Groshans made observations on this subject. G. L. Clark studied the relation between the at. vol. and the stability. A. E. H. Tutton gave

2·243 for the sp. gr. at 20°/4°, and 216·53 for the mol. vol. The indices of refraction are :

	Li-line.	*C*-line.	Na-line.	Tl-line.	Cd-line.	*F*-line.	*G*-line.
α . .	1·5246	1·5251	1·5285	1·5320	1·5359	1·5360	1·5423
β . .	1·5382	1·5337	1·5370	1·5405	1·5425	1·5447	1·5510
γ . .	1·5419	1·5424	1·5460	1·5496	1·5517	1·5539	1·5602

H. Topsöe and C. Christiansen made some observations on this subject. A. E. H. Tutton found the sp. dispersions, $\mu_G - \mu_C$, for α, β, and γ to be respectively 0·0038, 0·0037, and 0·0038, and the mol. dispersions, 1·81, 1·84, and 1·84. The sp. refractions for the *C*-line, and the μ^2-formula, are respectively 0·1366, 0·1385, and 0·1404, and the mol. refractions 66·37, 67·27, and 68·19 respectively. The mol. refractions for the μ-formula are 113·70, 115·56, and 117·45. C. Schaefer and M. Schubert studied the ultra-red reflection spectrum. C. von Hauer said that the salt lost only 0·6 part of water at 100°. J. Ferguson found the press., *p* mm., in the equilibrium $(NH_4)_2Ni(SeO_4)_2.6H_2O \rightleftharpoons (NH_4)_2Ni(SeO_4)_2.2H_2O + 4H_2O$.

	28·3°	37·2°	43·6°	56·0°	63·2°	69·0°	77·0°
p . . .	7·0	2·0	3·2	8·2	13·9	20·3	32·2

C. von Hauer prepared **potassium nickel selenate,** $K_2Ni(SeO_4)_2.6H_2O$, from a soln. of the component salts. The crystals have the form of the corresponding sulphate ; and G. vom Rath gave for the axial ratios of the monoclinic crystals $a : b : c = 0·7454 : 1 : 0·5060$, and $\beta = 90° 52'$; A. E. H. Tutton gave 0·7467 : 1 : 0·5059, and $\beta = 104° 27'$; the topic axial ratios $\chi : \psi : \omega = 6·1677 : 8·2898 : 4·1786$. The (201)-cleavage is well-developed. The optic axial angles are :

	Li-line.	*C*-line.	Na-line.	Tl-line.	Cd-line.	*F*-line.
$2E$.	129° 12′	129° 17′	130° 3′	130° 54′	131° 20′	131° 46′
$2H_a$.	66° 12′	66° 10′	65° 58′	65° 45′	65° 34′	65° 27′
$2H_o$.	95° 43′	95° 39′	95° 12′	94° 42′	94° 39′	94° 1′
$2V_a$.	72° 45′	72° 45′	72° 48′	72° 51′	72° 53′	72° 56′

A rise of temp. of 50° increases the optic axial angle $2E$ by 3° 16′. H. Topsöe gave 2·539 for the sp. gr. ; and A. E. H. Tutton, 2·559 at 20°/4°, and for the mol. vol. 206·14. The indices of refraction are :

	Li-line.	*C*-line.	Na-line.	Tl-line.	Cd-line.	*F*-line.	*G*-line.
α . .	1·5142	1·5147	1·5181	1·5212	1·5232	1·5251	1·5314
β . .	1·5232	1·5237	1·5272	1·5305	1·5325	1·5344	1·5407
γ . .	1·5387	1·5392	1·5427	1·5464	1·5486	1·5507	1·5571

A rise of temp. of 55° decreased the refractive index 0·0018. H. Topsöe and C. Christiansen made some observations on this subject. A. E. H. Tutton gave for the sp. dispersions, $\mu_G - \mu_C$, for α, β, and γ respectively 0·0032, 0·0032, and 0·0033 ; and the mol. dispersions respectively 1·68, 1·71, and 1·77. The sp. refractions for the *C*-line and the μ^2-formula are respectively 0·1178, 0·1195, and 0·1225 ; and the mol. refractions respectively 62·14, 63·04, and 64·60—the mol. dispersions with the μ-formula are respectively 106·10, 107·96, and 111·10. C. Schaefer and M. Schubert studied the ultra-red reflection spectrum. C. von Hauer found that the salt loses 13·35 per cent. or 4 mols. of water at 100°. J. Ferguson found the dissociation press., *p* mm., for the reaction $K_2Ni(SeO_4)_2.6H_2O \rightleftharpoons K_2Ni(SeO_4)_2.2H_2O + 4H_2O$, are :

	29·9°	40·0°	48·0°	53·9°	64·1°
p . . .	11·9	25·3	46·4	63·9	119·0

A. E. H. Tutton prepared **rubidium nickel selenate,** $Rb_2Ni(SeO_4)_2.6H_2O$, in green, more or less tabular, monoclinic crystals having the axial ratios $a : b : c = 0·7395 : 1 : 0·5031$, and $\beta = 105° 20'$. The topic axial ratios are $\chi : \psi : \omega = 6·2533 : 8·4561 : 4·2542$. The $(\bar{2}01)$-cleavage is good. The optic axial angle $2E$ is too large for measurement ; the other angles are :

	Li-line.	*C*-line.	Na-line.	Tl-line.	Cd-line.	*F*-line.
$2H_a$.	74° 42′	73° 38′	74° 6′	73° 52′	73° 35′	73° 21′
$2H_o$.	87° 47′	87° 29′	87° 32′	87° 15′	87° 2′	86° 53′
$2V_a$.	82° 23′	82° 22′	82° 13′	82° 7′	82° 3′	81° 58′

The sp. gr. is 2·856 at 20°/4°, and the mol. vol., 216·96. The indices of refraction are:

	Li-line.	*C*-line.	Na-line.	Tl-line.	Cd-line.	*F*-line.	*G*-line.
α . .	1·5161	1·5166	1·5198	1·5231	1·5248	1·5268	1·5335
β . .	1·5253	1·5258	1·5291	1·5325	1·5342	1·5363	1·5429
γ . .	1·5351	1·5356	1·5390	1·5424	1·5443	1·5466	1·5534

A rise of 55° in temp. diminished the refractive index 0·0017. The sp. dispersions, $\mu_G - \mu_C$, for α, β, and γ are respectively 0·0029, 0·0030, and 0·0030, and the mol. dispersions 1·84, 1·81, and 1·86 respectively. The sp. dispersions for the *C*-line, and the μ^2-formula, are 0·1059, 0·1074, and 0·1091 respectively; and the mol. refractions, 65·59, 66·57, and 67·61 respectively. The mol. refractions for the μ-formula are 112·08, 114·17, and 116·30 respectively. J. Ferguson found the dissociation press., p mm., for the reaction $Rb_2Ni(SeO_4)_2.6H_2O \rightleftharpoons 4H_2O + Rb_2Ni(SeO_4)_2.2H_2O$, are:

	30·2°	38·2°	52·3°	62·0°	75·9°
p . . .	1·5	3·1	9·0	16·0	37·9

Emerald-green crystals of **cæsium nickel selenate,** $Cs_2Ni(SeO_4)_2.6H_2O$, were also prepared; the axial ratios of the holohedral, prismatic, monoclinic crystals are $a:b:c=0·7288:1:0·4993$, and $\beta=106° 11′$; the topic axial ratios are $\chi:\psi:\omega=6·3317:8·6878:4·3378$. The $(\bar{2}01)$-cleavage is good. The optic axial angle $2E$ is too large for measurement; the other angles are:

	Li-line.	*C*-line.	Na-line.	Tl-line.	Cd-line.	*F*-line.
$2H_a$.	76° 7′	76° 5′	76° 0′	75° 55′	75° 50′	75° 43′
$2H_o$.	88° 57′	88° 52′	87° 57′	87° 11′	86° 49′	86° 30′
$2V_a$.	82° 4′	82° 43′	83° 8′	83° 28′	83° 37′	83° 43′

The sp. gr. is 3·114 at 20°/4° and the mol. vol. 229·17. The indices of refraction are:

	Li-line.	*C*-line.	Na-line.	Tl-line.	Cd-line.	*F*-line.	*G*-line.
α . .	1·5358	1·5363	1·5395	1·5428	1·5447	1·5467	1·5533
β . .	1·5412	1·5417	1·5450	1·5483	1·5504	1·5525	1·5589
γ . .	1·5451	1·5456	1·5519	1·5526	1·5547	1·5568	1·5631

For 55° rise of temp., the refractive index α decreases 0·0013; β, 0·0016; and γ, 0·0018. The sp. dispersions, $\mu_G - \mu_C$, for α, β, and γ are respectively 0·0026, 0·0027, and 0·0027; and the mol. dispersions 1·88, 1·89, and 1·92. The sp. refractions for the *C*-line and the μ_2-formula are 0·1012, 0·1010, and 0·1016 respectively; and the mol. refractions respectively 71·49, 72·09, and 72·52. The mol. refractions for the μ-formula are 122·90, 124·14, and 125·03 respectively. J. Ferguson found the dissociation press., p mm., for the reaction $Cs_2Ni(SeO_4)_2.6H_2O \rightleftharpoons 4H_2O + CsNi(SeO_4)_2.2H_2O$, are:

	30·2°	38·2°	52·3°	62·0°	75·9°
p . . .	15·8	26·8	59·4	95·5	157·4

L. C. Lindsley and L. M. Dennis prepared **thallous nickel selenate,** $Tl_2Ni(SeO_4)_2.6H_2O$; it is dehydrated at 120°, and then becomes yellow. A. E. H. Tutton gave for the axial ratios of the monoclinic crystals, $a:b:c=0·7456:1:0·5019$, and $\beta=105° 36′$. The cleavage is parallel to $(\bar{2}01)$. The topic axial ratios are $\chi:\psi:\omega=6·2680:8·4066:4·2193$; the sp. gr., 3·993 at 20°/4°; and the mol. vol., 214·13. The optic axial angles, and the indices of refraction, are:

	Li-	*C*-	Na-	Cd-	*F*-	*G*-light.
$2V$.	58° 5′	58° 10′	58° 59′	59° 51′	60° 17′	60° 53′
$2E$.	107° 24′	107° 31′	107° 20′	112° 3′	114° 10′	115° 38′
α .	1·6334	1·6339	1·6378	1·6443	1·6480	1·6523
β .	1·6454	1·6459	1·6498	1·6563	1·6600	1·6643
γ .	1·6512	1·6517	1·6560	1·6626	1·6666	1·6709

The formula for β is $1{\cdot}6504+882286\lambda^{-2}+30390800000000\lambda^{-4}+\ .\ .\ .$; for α, 1·6504 is diminished by 0·0120 ; and for γ, it is raised by 0·0062. The mol. refractions by the μ-formula, for α, β, and γ, are respectively 135·74, 138·31, and 139·56 ; the sp. refractions by the μ^2-formula are respectively 0·0895, 0·0909, and 0·0915, and the mol. refractions, respectively 76·56, 77·71, and 78·26.

K. Hradecky[16] obtained **palladious selenate,** $PdSeO_4$, by dissolving palladium in a mixture of selenic and nitric acids. It forms dark brownish-red, hygroscopic, rhombic prisms of sp. gr. 6·5. When warmed with conc. hydrochloric acid chlorine is evolved. It forms double salts with ammonium sulphate and ammonium selenate –**ammonium palladious selenate**—when a mixture of the two salts is crystallized from a soln. in conc. hydrochloric acid. Palladous selenate softens at a red-heat and then decomposes. K. Hradecky also found that cold selenic acid has no appreciable action on osmium at ordinary temp., but at 120° the element forms a colourless soln. which contains selenious acid and osmium tetroxide, but no *osmium selenate.*

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§ 13. Selenium Halides

G. J. Knox[1] passed selenium vapour over lead fluoride, melted in a platinum tube, and obtained selenium fluoride which can be volatilized without decomposition, and dissolved in conc. hydrofluoric acid. H. Moissan also said that selenium is attacked by fluorine in the cold; there are abundant white fumes, and the selenium soon melts and takes fire. Around it there is condensed a white crystalline compound which is decomposed by water, and dissolved by hydrofluoric acid. E. B. R. Prideaux prepared **selenium hexafluoride,** SeF_6, by the action of fluorine on selenium contained in a glass tube kept at −78°; this tube was joined to a second tube in which a white, crystalline solid was collected. This tube, while still in the freezing mixture, was sealed off. When the temp. is allowed to rise, the contents of the tube melt to a clear liquid and then pass into the gaseous condition. Analyses and mol. wt. determinations agreed with the formula SeF_6. The sp. gr. of the liquid at −28° is 2·51, and the mol. vol. 77·2. The vap. press. of the liquid becomes 760 mm. at −34·5°, corresponding with the b.p.; the m.p. is −39°; and the critical temp., 72·35°. E. Q. Adams studied the relations between the b.p. and composition. The coeff. of thermal expansion of the liquid between −3·5° and 51° is 0·032. The refractive index of the gas is 1·895. The index of refraction 1·000911 shows no approach to the value 1·001358 required by the additive law. There is a regularity in the indices of refraction of the gases of the same family of elements. The gas attacks mercury like ozone does. P. Lebeau said that the gas obtained by the action of fluorine on selenium in glass vessels is a gaseous mixture containing what is probably an oxyfluoride, but W. Ramsay added that the density of the gas 97·23 is not in agreement with either $SeOF_4$—density 83·5—or with SeO_2F_4—density 74·5. P. Lebeau found that the supposed gaseous hexafluoride is a mixture since by fractionation it can be separated into products of different density. The gaseous product, purified by liquefaction and vaporization, has a composition approximating the hexafluoride, but it always contains a little oxyfluoride; and after being manipulated in contact with glass and mercury, the gas has a higher degree of purity than before. If the fluorine acts on selenium in a copper vessel, **selenium tetrafluoride,** SeF_4, is formed. P. Lebeau added that this is not due to the reduction of the hexafluoride by copper, as suggested by W. Ramsay, because the same product is obtained with platinum vessels, and when fluorine acts on selenium in the presence of glass. E. B. R. Prideaux and C. B. Cox prepared selenium tetrafluoride by the action of dry silver fluoride on selenium tetrachloride. The first reaction is violent, and the distillation of the product gives a colourless, fuming liquid. The first fraction was deep red, and was thought to contain *selenium monofluoride*, Se_2F_2. According to P. Lebeau, selenium tetrafluoride is a colourless, intensely irritating liquid, boiling a little above 100°, and forming a white, crystalline solid at −80°; its vapour colours a Bunsen flame intensely blue. E. B. R. Prideaux and C. B. Cox found that the sp. gr. is rather greater than that of a corresponding mixture of selenium dioxide and hydrogen fluoride. The boiling starts at 91°–95°, stops, and recommences at 124°. This is the b.p. of the oxyfluoride, and hence the small quantity of liquid used in the determination had been hydrolyzed. The liquid solidified at −90°; the m.p. is −13·5°. According to P. Lebeau, the tetrafluoride attacks glass energetically, is decomposed by water, forming selenious and hydrofluoric acids, does not absorb fluorine, dissolves iodine, giving a reddish soln., and does not attack boron, silicon, or carbon on boiling. E. B. R. Prideaux and C. B. Cox found that the tetrafluoride reacts in the cold with crystalline silicon, forming selenium and silicon tetrafluoride; it does not react with sulphur in the cold; it reacts with red phosphorus, forming phosphorus trifluoride and oxytrifluoride. P. Lebeau also observed that with phosphorus there is a vivid reaction, selenium and phosphorus fluoride being formed. The fluoride is decomposed by alkali metals, and it attacks mercury in the cold, but is without action on platinum.

J. J. Berzelius[2] observed that when chlorine is passed over selenium, combination occurs with the evolution of heat, and brown **selenium monochloride,** Se_2Cl_2, is formed; as the chlorine continues its action, *selenium tetrachloride*, $SeCl_4$, is obtained as a white solid. R. Hanslian could not prepare *selenium dichloride*, $SeCl_2$; nor could R. Hanslian, and H. Rose obtain a *selenium hexachloride*, $SeCl_6$. According to E. Beckmann and R. Hanslian, when selenium and chlorine are mixed in molar proportions at −80°, and the mixture allowed to warm up to room temp., and then heated to 100°, a mixture of both the monochloride and tetrachloride is formed. If the proportions of the two elements correspond with the dichloride, a mixture of mono- and tetra-chloride is formed. J. J. Berzelius found that selenium converts the tetrachloride into the monochloride. F. Sacc, R. Hanslian, and W. Ramsay prepared the monochloride by the action of chlorine on selenium. A. Baudrimont obtained the monochloride by the action of phosphorus pentachloride on selenium, or on the selenide of phosphorus or antimony; A. Michaelis, by the action of phosphorus pentachloride on an excess of selenium dioxide, or oxychloride; A. Baudrimont, by the action of phosphorus trichloride on selenium tetrachloride; B. Rathke, by replacing the sulphur in sulphur monochloride with selenium; V. Lenher, by the action of the metals on selenium oxychloride; and E. Divers and M. Shimose, by the action of hydrogen chloride on a soln. of selenium in fuming sulphuric acid. V. Lenher and C. H. Kao showed that the monochloride can be produced in the presence of a large proportion of water. They concluded that when a soln. of selenium dioxide in conc. hydrochloric acid (36–37 per cent.) is treated with sulphur dioxide gas a yellow colour is produced when a relatively small amount of selenium dioxide is used, but when a high conc. of selenium dioxide is used, the red, oily liquid, Se_2Cl_2, separates. When selenium dioxide is dissolved in conc. hydrochloric acid and elementary selenium is added, large quantities of the monochloride are formed and separate as a red-brown oil. When selenium dioxide and selenium are suspended in either carbon tetrachloride or carbon disulphide and treated with hydrogen chloride, selenium monochloride is produced and passes into soln. in the carbon tetrachloride or disulphide. When a soln. of selenium in selenium oxychloride is treated with hydrogen chloride, selenium monochloride separates. When a mixture of selenium and selenium dioxide is added to conc. sulphuric acid and conc. hydrochloric acid is added the monochloride is produced. The addition of sulphuric acid to a soln. of selenium dioxide in hydrochloric acid precipitates white selenium tetrachloride which will react with elementary selenium if added to the mixture, forming the monochloride. When a sat. soln. of selenium dioxide in conc. hydrochloric acid (36–37 per cent.) is treated with sulphur dioxide, a small quantity of the monochloride is formed, but when this mixture is treated with conc. sulphuric acid, a large quantity of the monochloride appears. The use of phosphorus pentoxide as a dehydrating agent is also possible, but phosphorus pentoxide in this reaction possesses no advantages over sulphuric acid nor do such dehydrating agents as calcium chloride and zinc chloride. The monochloride can be purified by dissolving it in fuming sulphuric acid, reprecipitating with hydrogen chloride, and washing with sulphuric acid. The last traces of acid can be removed by treatment with dehydrated barium chloride. E. Divers and M. Shimose suggested potassium chloride as the deacidifying agent, but V. Lenher said that the alkali sulphates are slightly soluble in selenium monochloride, whereas neither barium chloride nor sulphate is soluble in that menstruum.

J. J. Berzelius described the crude monochloride as a brownish-yellow oil, heavier than water; E. Divers and M. Shimose said that it is a deep red liquid which smells like sulphur monochloride but not so strongly as sulphur monochloride; the **specific gravity** is 2·906 at 17·5°; V. Lenher and C. H. Kao found that if the liquid be freed from dissolved selenium and alkali salts, the sp. gr. is 2·7741 at 23°/4°. E. Divers and M. Shimose found that the monochloride is somewhat volatile at ordinary temp., and it sublimes in warm weather. At 100°, there is partial dissociation, forming an orange-red vapour. E. Beckmann and R. Hanslian said that the reddish-brown liquid decomposes to a considerable extent when distilled in vacuo—the tetrachloride collects with the distillate, and free selenium remains in the retort. E. P. Evans and W. Ramsay found the **vapour density** to be 7·1 in agreement with the assumption that no dissociation occurs. C. Chabrié found 7·69–8·12 when the theoretical value for Se_2Cl_2 is 7·95. F. P. Evans and W. Ramsay said that the monochloride decomposes when distilled: $2Se_2Cl_2{=}SeCl_4+3Se$; accordingly, E. Divers and M. Shimose represented the constitution by $Se{=}Se{=}Cl_2$. Analyses were made by F. Sacc, and E. Divers and M. Shimose. E. Beckmann and R. Hanslian found that the f.p. of soln. in ethylene dibromide corresponds with Se_2Cl_2; and that the monochloride does not solidify at —78°; this is due to undercooling because V. Lenher and C. H. Kao gave —85° for the **melting point**; and 130° for the **boiling point.** J. Thomsen gave for the **heat of formation** from amorphous selenium: $(2Se,Cl_2)=22\cdot15$ Cals. D. Gernez observed that the **spectrum** of the vapour shows lines which begin in the blue and end in the green; and they are continued in the ultra-violet. V. Lenher and C. H. Kao gave 1·59617 for the **index of refraction** at 25°; and $0\cdot0_6512$ mhos for the sp. **electrical conductivity.** A. Voigt and W. Biltz found it to be a bad conductor, and gave, at 18°, $0\cdot0_221$ mhos.

F. Krafft and O. Steiner, and A. von Bartal compared the properties of the corresponding selenium, sulphur, and tellurium compounds. V. Lenher and C. H. Kao said that the properties of the monochloride, in general, are those of a typical acid chloride and a strong chlorinating agent. **Hydrogen** has no action on selenium monochloride; and J. J. Berzelius added that it is decomposed by **water** into hydrogen chloride, selenium, and selenious acid: $2Se_2Cl_2+2H_2O=SeO_2+3Se+4HCl$, an equation confirmed by the work of R. Hanslian. E. Divers and M. Shimose said that water decomposes it slowly into selenium and selenium tetrachloride. E. Beckmann and R. Hanslian showed that the action of an excess of **chlorine** forms only the tetrachloride. E. Beckmann found that selenium monochloride is insoluble in liquid **bromine**; R. Hanslian, that it reacts vigorously with boiling bromine; and V. Lenher and C. H. Kao, that **iodine** is freely soluble in the liquid, forming a soln. which is scarcely black, and containing 25·48 per cent. of iodine; the soln. has a sp. gr. 93·1597 at 25°. When selenium monochloride is treated with an excess of **iodic acid,** or of **potassium chlorate, bromate, or iodate,** the halogen is liberated, and selenium dioxide is formed; and no reaction occurs with **potassium perchlorate,** even when the monochloride is heated. E. Divers and M. Shimose said that only a little **sulphur** is slowly dissolved by the monochloride; on the other hand, V. Lenher and C. H. Kao found that 100 parts of the monochloride will dissolve 48·81 parts of sulphur, forming a viscid liquid. B. Rathke showed that some sulphur in sulphur monochloride can be displaced by selenium, and V. Lenher and C. H. Kao showed that the reaction is $S_2Cl_2+2Se\rightarrow Se_2Cl_2+2S$; while with **hydrogen sulphide** there is a slow reaction with the evolution of heat, and the formation of hydrogen chloride, sulphur, and selenium. Dry **sulphur dioxide** does not react with selenium monochloride even at its b.p. E. Divers and M. Shimose observed that with **sulphur trioxide** the monochloride forms a green soln. having the composition $S_2Cl_2.SO_3$—*vide infra*—which reacts with hydrochloric acid, forming, according to V. Lenher and C. H. Kao, selenium monochloride, chlorosulphonic acid, and sulphurous acid. F. P. Evans and W. Ramsay found that selenium tetrachloride dissolves **selenium** until the soln. contains 80 per cent. selenium, which is more than is present in the monochloride. V. Lenher and C. H. Kao found that 100 parts of selenium monochloride at 25° dissolve 9·73 parts of selenium, and the soln. contains 71·85 per cent. of selenium. The rate of soln. is slow in the cold, and requires frequent shaking for equilibrium; B. Rathke, and V. Lenher and M. Shimose found that the hot liquid, when sat., deposits, on cooling, crystals of black selenium. Selenium oxychloride dissolves selenium, and selenium monochloride dissolves **selenium dioxide**; and the reaction: $2Se_2Cl_2+SeO_2\rightleftharpoons 2SeOCl_2+3Se$, is reversible; the products of the reaction can be separated by carbon tetrachloride. Selenium monochloride reacts with **tellurium,** forming tellurium tetrachloride, and liberating selenium; the same products are obtained with **tellurium dichloride**; while with **tellurium dioxide,** selenium, and selenium oxychloride are formed.

W. Strecker and L. Claus observed that liquid **ammonia** has a vigorous action on selenium monochloride which results in the deposition of red selenium; and similarly if the monochloride be mixed with chloroform or anhydrous benzene—only traces of selenium nitride are produced. If the monochloride be in ethereal soln., **selenium chloronitride,** Se_2NCl, is formed. A. Baudrimont found that

phosphorus reacts with selenium monochloride, forming selenium and phosphorus trichloride. V. Lenher and C. H. Kao added that while red phosphorus reacts slowly with the monochloride, white phosphorus explodes. No pentachloride is formed. A. Baudrimont, and V. Lenher and C. H. Kao observed that an excess of **phosphorus pentachloride** reacts, forming a red solid, $SeCl_4.PCl_5$, but no phosphorus selenochloride. V. Lenher and C. H. Kao found that **arsenic** reacts in the cold, forming arsenic trichloride and selenium, and similarly also with **arsenic triselenide ; arsenic trisulphide** reacts at 100°, forming the trichloride, sulphur, and selenium ; **arsenic trioxide** gives the trichloride, selenium, and selenium oxychloride ; **antimony** forms the pentachloride with an intermediate formation of selenide ; **antimony trichloride** is oxidized to pentachloride which then reacts with more selenium monochloride to form $SeCl_4.2SbCl_5$. In many other cases, selenium monochloride reacts as if it were a mixture of selenium and selenium tetrachloride. The monochloride reacts with **antimony trisulphide** at 100°, forming the trichloride, selenium, and sulphur, with **antimony trioxide,** forming the trichloride, and selenium oxychloride, with **bismuth,** forming the trichloride and selenium ; with **bismuth selenide,** forming the same products ; with **bismuth sulphide,** at 100°, forming the trichloride, selenium, and sulphur ; and with **bismuth trioxide,** forming the trichloride, selenium, and selenium oxychloride.

E. Divers and M. Shimose found that **alcohol** slowly decomposes selenium monochloride into selenium and selenium tetrachloride ; and similarly also with **ether.** Its action on **aliphatic hydrocarbons** was studied by H. W. Bausor and co-workers, F. H. Heath and W. L. Semon, and C. E. Boord and F. F. Cope. H. W. Bausor and co-workers found that while sulphur monochloride reacts with ethylene : $2(CH_2 : CH_2)+S_2Cl_2=(CH_2Cl.CH_2)_2S+S$, selenium monochloride reacts : $2(CH_2 : CH_2)+2Se_2Cl_2=(CH_2Cl.CH_2)_2SeCl_2+3Se$, presumably on account of the ready decomposition of selenium monochloride into chlorine and selenium. According to V. Lenher and C. H. Kao, selenium monochloride is immiscible with pentane, hexane, and heptane. V. Lenher and C. H. Kao said that it is miscible with the **aromatic hydrocarbons,** benzene, toluene, and the xylenes—C. Chabrié studied its action on benzene with iron as catalyst. V. Lenher and C. H. Kao found that separations of the **hydrocarbons** by selenium monoxide are not possible. Substances like **hair, silk, wool,** and **leather,** containing carbohydrates and proteins are not readily attacked ; while **gliadin** from wheat, and **elastin** as well as albumen are not dissolved ; **cellulose** is not appreciably attacked ; **vegetable and fish oils** react like sulphur monochloride, precipitating selenium and forming a rubber-like substance ; pure or vulcanized **rubber** is slowly acted upon—slowly in the cold but more rapidly when heated ; **bakelite** is soluble in warm selenium monochloride ; and **coal** of the bituminous type, dried at 160°, is but little affected. W. Strecker and A. Willing observed the action of selenium monochloride on organic magnesium compounds. V. Lenher and C. H. Kao said that selenium monochloride slowly attacks **silicon,** forming silicon tetrachloride and selenium.

V. Lenher and C. H. Kao found that **sodium** slowly reacts with selenium monochloride, forming sodium chloride and selenium, but the reaction soon stops owing to the formation of a protective film of insoluble sodium chloride. When the system is heated, the action proceeds with the evolution of light and heat. When **potassium** is added to selenium monochloride at ordinary temp., the mixture explodes violently, forming potassium chloride and selenium. With an excess of **copper,** the selenide and chloride are formed, and with the selenium monochloride in excess, cupric chloride and selenium. W. W. Taylor and co-workers represented the reaction : $Se_2Cl_2+5Cu=2Cu_2Se+CuCl_2$. V. Lenher and C. H. Kao said that an excess of the monochloride also forms cupric chloride when treated with **cuprous and cupric selenides.** W. W. Taylor represented the reaction with an excess of monochloride : $2Cu_2Se+4Se_2Cl_2=4CuCl_2+10Se$. According to V. Lenher and C. H. Kao, an excess of **silver** forms the chloride and selenide, otherwise, silver chloride and selenium ; **silver selenide** forms silver chloride and selenium ; **mag-**

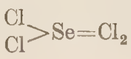
nesium forms magnesium chloride and selenium, and if the metal is in excess some selenide may be formed; **zinc and cadmium** are tarnished on the surface when heated for 5 months with the monochloride, but zinc dust takes fire when introduced into the monochloride, forming zinc chloride and selenide, selenium, and selenium oxychloride when the metal is in excess, if otherwise, no selenide is formed; **zinc selenide** forms chloride and selenium; **mercury** vigorously reacts when warm, forming the selenide and chloride if the mercury is in excess, and if otherwise, mercuric chloride and selenium are formed; **mercuric selenide** is attacked by the monochloride, forming mercuric chloride and selenium; **aluminium** is not attacked in the cold, but at 80° the metal burns brilliantly, forming aluminium chloride and selenide if the metal is in excess, otherwise selenium and aluminium chloride are formed—if a mixture of aluminium and selenium monochloride are heated for 12 hrs., $2AlCl_3.SeCl_4$ is produced, showing that the monochloride is decomposed into selenium and selenium tetrachloride; **aluminium selenide** forms the chloride and selenium; **tin,** and **tin selenide** form stannic chloride and selenium; **lead** is attacked only slowly; **chromium** is tarnished superficially when heated with selenium monochloride for 5 months; **manganese** is attacked only slowly; **iron** forms ferric chloride and selenium; **iron selenide** forms ferric chloride and selenium; **nickel** is not tarnished or attacked at 100° during 5 months, and the **nickel selenide** is only slowly converted into chloride; and the action on **cobalt,** and **cobalt selenide** is similar to the case with nickel.

V. Lenher and C. H. Kao found that **sodium dioxide** reacts violently with the evolution of light and heat when it is treated with monochloride, forming sodium chloride, selenite, selenate, and free selenium. **Potassium tetroxide** reacts still more violently, forming analogous products; lithium oxide yields the selenite and chloride and selenium; **copper oxide** yields the chloride and selenium, and if selenium monochloride is in excess, selenium oxychloride is formed; **silver oxide** reacts in an analogous way; **calcium oxide** is slowly converted into chloride, and selenium oxychloride and selenium are formed—similarly also with **strontium oxide,** and **barium oxide; beryllium oxide** yields the chloride, selenium oxychloride, and selenium; **magnesium oxide** behaves similarly; **cadmium oxide** is only partially attacked during some months' action; **zinc oxide** reacts, forming the chloride, selenium, and selenium dioxide if the oxide is in excess, and zinc chloride, selenium oxychloride, and selenium when the monochloride is in excess; **mercuric oxide** behaves in an analogous manner; **lead monoxide** reacts slowly, forming lead chloride, selenium, and selenium oxychloride; **lead dioxide** forms similar products, but the action is rapid; **ferric oxide** forms analogous products; **cobalt oxide** acts slowly, forming the chloride; and similarly also with **nickel oxide.** No reaction occurs when the monochloride is heated with **potassium chromate** or **dichromate,** or with **potassium permanganate.**

V. Lenher and C. H. Kao found that the lower **metal chlorides** are chlorinated to a higher stage. Potassium chloride is slightly soluble in selenium monochloride; cuprous chloride is oxidized to cupric chloride; magnesium chloride adsorbs the monochloride; aluminium chloride forms the complex $2AlCl_3.SeCl_4$; and stannous chloride forms stannic chloride. The **metal sulphides** are usually attacked, forming the corresponding chlorides, selenium, and sulphur; copper, silver, zinc, cadmium, and aluminium sulphides react readily at ordinary temp., while those of magnesium, mercury, tin, and iron react at 100°; those of lead and nickel act only slowly on warm selenium monochloride; while those of calcium and barium are only slightly attacked by the warm monochloride during a week's action. The **metal carbonates** are often chlorinated; thus, fused sodium and potassium carbonates are readily attacked, forming the respective chlorides, selenium oxychloride, carbon dioxide, and selenium, as do dry lithium carbonate and silver carbonate. Basic copper carbonate gives cupric chloride. Magnesium basic carbonate is not attacked in the cold, but when heated to 130° in the vapour of selenium monochloride, it is attacked, giving carbon dioxide. The carbonates of calcium, strontium, and barium give no carbon dioxide in 24 hrs. in the cold, but when moistened with water they give the calculated yield of carbon dioxide in a few minutes. Zinc carbonate gives the chloride and carbon dioxide. Cadmium carbonate is not attacked. The carbonates of lead and manganese are not attacked in the cold. The mineral siderite ($FeCO_3$) is not attacked. The basic carbonates of nickel and cobalt are only very slowly attacked even when heated.

J. J. Berzelius obtained **selenium tetrachloride,** $SeCl_4$, as indicated above, by the action of an excess of chlorine on selenium, or of chlorine on selenium monochloride. F. P. Evans and W. Ramsay, and F. Clausnizer used this mode of preparation. The product was washed with carbon disulphide to remove chlorine, and then dried in a current of warm, dry air. H. Rose found that when a mixture of a selenate, sodium chloride, and conc. sulphuric acid is heated, a mixture of chlorine and selenium tetrachloride is first evolved, and afterwards selenium dioxide and sulphuric acid. B. Rathke obtained some tetrachloride by heating selenium dioxide with hydrochloric acid; and A. Michaelis, by the action of thionyl chloride or of phosphorus trichloride on selenium oxychloride, of 13 parts of phosphorus pentachloride on 7 parts of selenium dioxide; a mixture of selenium oxychloride and phosphoryl chloride is first formed, and this then furnishes phosphorus pentoxide and selenium tetrachloride. The solid product was warmed in a current of carbon dioxide to remove phosphoryl chloride; and the residue, when heated still more, furnished a sublimate of selenium tetrachloride while phosphorus pentoxide remained. The phosphoryl chloride, which is first distilled over when condensed and allowed to stand some time, may deposit crystals of selenium tetrachloride. A. Baudrimont prepared the tetrachloride by the action of phosphorus pentachloride on lead selenide; V. Lenher and H. B. North, by melting a mixture of thionyl chloride and selenium dioxide: $SeO_2+2SOCl_2=SeCl_4+2SO_2$; and by the action of selenium on sulphuryl chloride: $Se+2SO_2Cl_2=SeCl_4+2SO_2$; and A. B. Lamb, by the action of anhydrous selenic acid on acetyl chloride at 0°—the yield is almost quantitative. C. Chabrié purified selenium tetrachloride by repeated sublimation at 170°–180° in a current of chlorine, and obtained fine crystals. R. Hanslian used a similar process.

J. J. Berzelius described it as a white solid; F. P. Evans and W. Ramsay obtained it in pale yellow crystals. A. Michaelis obtained cubic crystals from a soln. of the tetrachloride in hot phosphoryl chloride. J. J. Berzelius said that the tetrachloride volatilizes without melting, and this more easily than the monochloride, forming a yellow vapour which condenses to a mass of white crystals. F. Clausnizer said that the vap. density is 3·92 when the theoretical value for $SeCl_4$ is 7·63. This shows that the dissociation $2SeCl_4=Se_2Cl_2+3Cl_2$ probably occurs. He added that the yellow vap. darkens in colour as the temp. is raised. C. Chabrié gave 3·78–3·85 for the vap. density at 360°. F. P. Evans and W. Ramsay referred the vap. density to hydrogen unity when the theoretical value for $SeCl_4$ is 110·2; and they found 110·25 at 180°; 111·76 at 200°; 84·20 at 225°; 72·82 at 295°; and 66·49 at 350°. They inferred that no marked dissociation occurs below 200°, but, above this temp., dissociation may occur as indicated above, or according to $2SeCl_4=Se+4Cl_2$—in both cases the vol. is doubled; at about 288°, the tetrachloride is dissociated. Observations were also made by A. Kekulé. E. Beckmann and R. Hanslian made cryoscopic observations on soln. of the tetrachloride in acetic acid and in phosphoryl chloride, but with unsatisfactory results for mol. wt. determinations. J. Thomsen found the heat of formation of the solid tetrachloride from its elements to be 46·16 Cals., and the heat of soln. in water, 30·37 Cals. H. Becquerel gave for the index of refraction, 1·8070; and the magnetic rotation of the plane of polarized light, 2·408. E. B. R. Prideaux, by analogy with selenious acid, $(HO)_2=Se=O$, represented the constitution by the formula:



$$\begin{matrix}Cl\\Cl\end{matrix}\!>Se=Cl_2$$

A. Voigt and W. Biltz could not measure the conductivity of the fused chloride owing to its decomposition.

J. J. Berzelius found that heat is developed when selenium tetrachloride comes in contact with **water,** and the reaction is symbolized: $SeCl_4+2H_2O=4HCl+SeO_2$; this was confirmed by E. Beckmann and R. Hanslian. R. Weber added that with only a small proportion of water, or on exposure to moist air, selenium oxychloride is formed. E. Beckmann and R. Hanslian said that an excess of **chlorine** does not form a higher chloride. E. Beckmann said that the tetrachloride is insoluble in liquid **bromine;** R. Weber, that **hydrogen sulphide** forms hydrogen chloride and selenium sulphide. A. W. Ralston and J. A. Wilkinson showed that liquid hydrogen sulphide at low temp. reacts slowly with selenium tetrachloride, forming selenium monochloride, and at room temp., red selenium is formed. R. Weber found that dry **sulphur dioxide** does not act on the hot tetrachloride; W. Prandtl and P. Borinsky, H. Rose, and F. Clausnizer observed that with **sulphur trioxide** there is formed a complex $SO_3.SeCl_4$—*vide infra;* F. Clausnizer, that with **sulphuric acid** the reaction can be symbolized: $3SeCl_4+2H_2SO_4=SeO_2+2(SO_3.SeCl_4)+4HCl$, while part reacts $3SeCl_4+2H_2SO_4=SeOCl_2+H_2S_2O_7+2HCl$, followed by $SeOCl_2+2H_2SO_4=SeO_2+H_2S_2O_7+2HCl$; with **pyrosulphuric acid,** the reaction is symbolized: $H_2S_2O_7+SeCl_4=H_2SO_4+SO_3.SeCl_4$; with **chlorosulphonic acid** there is formed $SO_3.SeCl_4$; and with **pyrosulphuryl chloride** the reaction can be symbolized: $S_2O_5Cl_2+SeCl_4=SO_2+Cl_2+SO_3.SeCl_4$. R. Weber found that with **selenium dioxide** there is formed selenium oxychloride. According to V. Lenher, when **tellurium dioxide** and selenium tetrachloride are brought together in mol. proportions and heat is applied, reaction takes place between the two. Quite a high temp. is necessary to start the reaction, but when once begun, it proceeds readily. Selenium oxychloride first distils at its f.p., and, on raising the temp. to a little below 400°, tellurium tetrachloride distils, while tellurium remains as a non-volatile residue. The reaction probably proceeds as follows, $2SeCl_4+TeO_2=2SeOCl_2+TeCl_4$. R. Espenschied showed that when dry **ammonia** acts on selenium tetrachloride there is formed ammonium chloride, selenium, nitrogen, and hydrogen; and if the ammonia is dil. with an inert gas, and the temp. low, nitrogen selenide is formed. A. Verneuil said that if dry ammonia acts on selenium tetrachloride suspended in carbon disulphide, nitrogen selenide is formed. W. Strecker and L. Claus observed that liquid ammonia, in the absence of a solvent, behaves towards the tetrachloride as it does towards the monochloride; in the presence of carbon disulphide a pale yellow, amorphous solid is formed which is difficult to purify. A. Baudrimont found that **phosphorus** forms phosphorus selenide, and, if in excess, selenium and phosphorus trichloride; while **phosphorus tetrachloride** forms the complex $2PCl_5.SeCl_4$ -the same compound is produced by the action of phosphorus trichloride on selenium monochloride. A. Michaelis said that the tetrachloride is soluble in hot **phosphoryl chloride.** R. Weber observed that **arsenic trioxide** is converted into the trichloride, etc. A. Michaelis said that the tetrachloride is insoluble in carbon disulphide, and since the monochloride is soluble, F. P. Evans and W. Ramsay said that it is possible to separate the two selenium chlorides by means of this agent. F. Clausnizer observed that selenium monochloride has very little action on **acetic acid** at ordinary temp., but when warmed, the liquid becomes brown, hydrogen chloride is evolved, and selenium monochloride is formed. Chloro-substitution products of acetic acid are also produced. G. T. Morgan and co-workers studied the action of the tetrachloride on the diketones, and triketones, and on ethylene. W. W. Taylor and co-workers represented the reaction with **copper** by the equation: $2SeCl_4+3Cu=3CuCl_2+Se_2Cl_2$, and for the action of this product on copper, *vide supra.* Attempts by W. Muthmann and J. Schäfer to prepare **chloroselenates** analogous to the bromoselenates (*q.v.*) furnished chloropyroselenites—*vide infra.*

According to G. S. Sérullas,[3] selenium and bromine are miscible in various proportions, but the 1 : 5 mixture appears to be the most stable; bromine rapidly unites with powdered selenium, and the combination is attended by a hissing noise, and the evolution of much heat. The product quickly solidifies to a brownish-red mass interspersed with particles of a yellow colour. When exposed to air, the product emits an odour resembling that of sulphur chloride; when heated it partly sublimes unchanged, and partly decomposes into bromine and selenium; it dissolves completely in water with the exception of a few flakes of selenium, and the colourless soln. contains hydrobromic and selenious acids. G. S. Sérullas's product was probably impure *selenium tetrabromide*, $SeBr_4$. R. Schneider prepared **selenium monobromide,** Se_2Br_2, by mixing 15·9 parts of selenium with 16 parts of bromine. Much heat is developed during the reaction; and it is better to drop the bromine on the large pieces of selenium, or to add bromine to carbon disulphide, standing over powdered selenium, until the selenium is almost all converted to bromide. It is also produced by mixing 5 parts of the tetrabromide with 3 parts of selenium. V. Lenher and C. H. Kao obtained the monobromide by treating selenium dioxide with hydrobromic acid—obtained by the action of bromine on sulphurous acid.

> Bromine (135 c.c.) is gradually added by means of a separatory funnel to a soln. of sulphur dioxide in ice water, sulphur dioxide being continuously passed into the soln. When the soln., which is a mixture of sulphuric and hydrobromic acids, is colourless it can be used directly for the preparation of the monobromide. Now, when 115 grms. of selenium dioxide are added, followed by 235 grms. of elementary selenium, the reaction starts at once with the production of the monobromide. About a litre of conc. sulphuric acid is added, and as the mixture cools the monobromide separates as a dark red oil, which may be further purified, if desired, by washing with conc. sulphuric acid. The yield is about 90 per cent.

R. Schneider described selenium monobromide as a dark, blood-red liquid, which appears to be almost black and opaque in thick layers, and in thin layers, ruby-red. The sp. gr. is 3·604 at 15°. It has an unpleasant smell resembling that of sulphur chloride. It partially decomposes when heated, just giving off bromine vapour, then selenium tetrachloride, and at 225°–230° the monobromide passes off, and finally selenium. At 80°, in a sealed tube, no sublimate of the tetrabromide is formed if neither selenium tetrabromide nor an excess of bromine is present. D. Gernez observed the line-spectrum of the vapour. According to R. Schneider, when the monobromide is exposed to moist air, a layer of selenious and hydrobromic acids is formed, and some selenium separates out. It sinks in water and slowly hydrolyzes: $2Se_2Br_2+2H_2O=3Se+SeO_2+4HBr$. It emits a hissing noise as it unites directly with bromine to form the tetrabromide. The monobromide mixes with carbon disulphide to form a reddish-brown liquid; it dissolves without decomposition in chloroform, and in ethyl bromide; it quickly decomposes absolute alcohol, especially if dissolved in carbon disulphide: $2Se_2Br_2=3Se+SeBr_4$; in aq. alcohol the reaction proceeds: $2Se_2Br_2+2H_2O=3Se+SeO_2+4HBr$; a soln. in ethyl iodide forms selenium iodide (*q.v.*), and ethyl bromide; silver cyanide forms selenium cyanide when added to a soln. of selenium monobromide in carbon disulphide. The monobromide is slowly decomposed by aq. ammonia, or potash-lye, but more rapidly by ammonium sulphide, which forms a brown soln. containing bromide and selenosulphide precipitated by hydrochloric acid. W. Strecker and L. Claus observed that liquid ammonia in the presence of ether forms **selenium bromodinitride,** Se_2N_2Br, otherwise its action is similar to that with the monochloride. A. Pieroni and co-workers studied the action of the monobromide on magnesium alkyl compounds.

As indicated above, G. S. Sérullas prepared impure **selenium tetrabromide,** $SeBr_4$; and R. Schneider obtained it by adding bromine to selenium to form the monobromide, and continuing the addition to convert this into the tetrabromide. The excess of bromine is removed by a current of dry air; the tetrabromide is decomposed by moist air. The tetrabromide is also prepared by the action of bromine on a soln. of the monobromide in carbon disulphide, chloroform, or ethyl bromide—the tetrabromide separates from conc. soln. as a yellow powder. Absolute alcohol transforms the monobromide into selenium and the tetrabromide.

W. Muthmann and J. Schäfer prepared the tetrabromide by dissolving selenium dioxide in hydrobromic acid: $SeO_2+4HBr=2H_2O+SeBr_4$. The brown colour of the liquid is due to the formation of some free bromine.

According to R. Schneider, selenium tetrabromide appears as a pale reddish-brown powder, which is crystalline if obtained from soln. with an excess of bromine, or from soln. in carbon disulphide. It has an unpleasant odour recalling that of sulphur chloride. It is volatile at ordinary temp., and when heated for a long time at 70°–80°, it is partially decomposed with the evolution of bromine, and the formation of selenium monobromide contaminated with the tetrabromide. A little tetrabromide sublimes in dark orange-red crystals. Selenium tetrabromide is decomposed by moist air into bromine and selenium monobromide; it forms a yellow soln. with a little water, but with more water the soln. is colourless, for the tetrabromide is completely hydrolyzed: $SeBr_4+2H_2O=SeO_2+4HBr$. It does not form a higher bromide when treated with an excess of bromine; it forms a brown soln. with hydrochloric acid; W. Prandtl and P. Borinsky found the reaction with sulphur trioxide furnishes $SOBr_2.SO_3$. R. Schneider found that the tetrabromide forms an oxybromide with selenium dioxide; it is partially decomposed by alcohol; it dissolves without decomposition in carbon disulphide, chloroform, and ethyl bromide. W. Strecker and L. Claus found that the action of liquid ammonia resembles that with the tetrachloride; but in the presence of carbon disulphide a better yield of selenium nitride is obtained.

According to W. Muthmann and J. Schäfer, if ammonium chloride be added to a hydrobromic acid soln. of selenium dioxide, garnet-red, octahedral crystals of **ammonium hexabromoselenate,** $(NH_4)_2SeBr_6$, are formed. V. Lenher prepared it by dissolving ammonium bromide (9 parts) in water, adding selenium (4 parts), and a slight excess of bromine until a clear soln. was obtained, and heating on the water-bath until the excess of bromine was expelled; on slow evaporation, crystals of ammonium bromoselenate separated, which were purified by repeated crystallization. The garnet-red crystals have a sp. gr. of 3·3266; and E. Carozzi gave 3·328. E. Carozzi found that the deep red octahedral crystals belong to the cubic system and they are isomorphous with ammonium stannic hexabromide, and ammonium platinum hexabromide. The crystals are decomposed by water, forming a soln. of the bromide, selenious acid, and hydrobromic acid. Ether slowly extracts selenium tetrabromide. The salt was also examined by A. Gutbier and W. Grünewald, who also prepared a number of complex salts—of the type R_2SeBr_4—with organic radicles. V. Lenher prepared corresponding salts with methylamine, dimethylamine, ethylamine, trimethylamine, tetraethylammonium, and pyridine salts; but not salts with aniline, diphenylamine, phenylhydrazine, or quinoline. J. F. Norris also prepared salts with the methylamines. A. Gutbier and W. Grünewald also prepared a number of these compounds. Neither W. Muthmann and J. Schäfer, nor V. Lenher, were able to prepare either *lithium hexabromoselenate,* Li_2SeBr_6, or *sodium hexabromoselenate,* Na_2SeBr_6; but **potassium hexabromoselenate,** K_2SeBr_6, was readily obtained. V. Lenher found that **rubidium hexabromoselenate,** Rb_2SeBr_6, and **cæsium hexabromoselenate,** Cs_2SeBr_6, are less soluble than the corresponding potassium salt. These three salts were also prepared by A. Gutbier and W. Grünewald. *Silver hexabromoselenate,* Ag_2SeBr_6, could not be prepared by W. Muthmann and J. Schäfer. P. Maier studied the crystallography of the aliphatic bromoselenates.

According to J. B. Trommsdorff,[4] when a mixture of eq. proportions of iodine and selenium is heated, the mass fuses. Alcohol extracts all the iodine from the dark grey product. R. Schneider obtained what he regarded as **selenium monoiodide,** Se_2I_2, in a similar manner; and also by heating a mixture of selenium monobromide and ethyl iodide. He said that the semi-metallic mass melts at 68°–70°, with the emission of a little iodine vapour. The product easily decomposes, giving off iodine vapour even at ordinary temp., and, at 100°, all the iodine is slowly evolved. The product is decomposed by water: $2Se_2I_2+3H_2O$

$=4HI+3Se+H_2SeO_3$, and the liquid gradually turns brown owing to a reaction between the hydriodic and selenious acids. The reaction made R. Schneider believe that a chemical compound and not a mixture is here involved. P. Guyot prepared what he called *un nouveau feu liquid* from a mixture of the two elements. R. Schneider said that if conc. selenious acid be decomposed by hydriodic acid, **selenium tetraiodide,** SeI_4, is formed: $H_2SeO_3+4HI=SeI_4+3H_2O$; the same product is obtained when eq. proportions of the two elements are fused together; and when ethyl iodide is treated with selenium tetrabromide: $SeBr_4+4C_2H_5I=SeI_4+4C_2H_5Br$. A small amount of a by-product smelling like cacodyl—*selenium ethide*—is thought to be formed. The colour is a darker grey than is the monoiodide. The tetraiodide melts at 75°–80°, forming a dark brown liquid. It loses iodine when heated, or when extracted with solvents. Water decomposes it as in the case of the monoiodide, but more slowly. G. Pellini and S. Pedrina showed that no chemical individuals are produced when the two elements are melted together because the f.p. curve is of the simple V-type—Fig. 62—with a eutectic at 58° corresponding in composition with the supposed monoiodide. No mixed crystals are formed excepting, perhaps, within very narrow limits. From the f.p. of mixtures of selenium in iodine, F. Olivari obtained mol. wts. of selenium in excess of that required for Se_2; and from the f.p. and b.p. of the soln., R. Hanslian obtained values rather less than that for $Se_2=158{\cdot}4$. R. Hanslian inferred from his observations that a true monoiodide is formed, and believed that G. Pellini and S. Pedrina's curve wants revision. R. Wright observed no evidence of the formation of solid soln. or of chemical compounds in his study of the vap. press. of fused mixtures of the two elements. E. Beckmann and C. Platzmann studied the depression of the f.p. of selenium, and mixtures of selenium and sulphur by iodine. In the case of sulphur in iodine, the mol. wt. is S_8, with selenium Se_2 to Se. There is no evidence of the formation of a compound of selenium and iodine, and the low mol. wt. of selenium in iodine has not been explained.

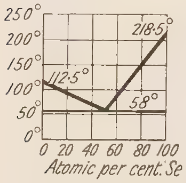


FIG. 62.—Freezing-point Curve of the System: Selenium-Iodine.

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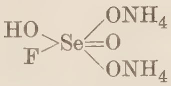
§ 14. Oxyhalogen Compounds of Selenium

E. B. R. Prideaux and C. B. Cox[1] prepared **selenium oxyfluoride,** $SeOF_2$, or selenyl fluoride, by the action of dry silver fluoride on selenium oxychloride in a platinum bottle, with subsequent distillation and condensation in a platinum condenser (water-cooled). It is a colourless, fuming liquid, with an ozone-like odour similar to that of some organic compounds which have been treated with fluorine. The sp. gr. is 2·67; the mol. vol., 49·2; the b.p., 124°; and the m.p., 4·6. There is no residue on distillation; and the behaviour of the salt is quite different from that of a mixture of selenium dioxide and hydrofluoric acid. The liquid rapidly attacks glass; and the action with powdered silica is violent: $2SeOF_2+SiO_2=2SeO_2+SiF_4$. Crystalline silicon is slowly attacked in the cold; rapidly when heated: $Si+2SeOF_2=SiF_4+SeO_2+Se$. The reaction with phosphorus is mainly in accord with $6SeOF_2+4P=4POF_3+SeO_2+5Se$. With sulphur there is no attack in the cold, but when warmed, a gas is evolved, and red selenium is deposited. Alcohol readily mixes with the liquid; carbon tetrachloride forms two layers.

R. F. Weinland and J. Alfa obtained **ammonium fluohydroxyselenate,** $(NH_4)_2SeO_3(OH)F$, or



by concentrating a soln. of ammonium selenate in an excess of hydrofluoric acid. It crystallizes in flat, rhombic prisms which quickly lose their lustre when exposed to air, and which are freely soluble in water, forming a strongly acid soln. By evaporating a soln. of potassium selenate in hydrofluoric acid over lime in a desiccator, **potassium hydrodifluodiselenate,** $K_3HSe_2O_7F_2.H_2O$, is formed in monoclinic crystals which quickly decompose on exposure to air with the loss of water and hydrogen fluoride, and then of oxygen, leaving a residue of selenate and selenium dioxide; similarly with **rubidium hydrodifluodiselenate,** $Rb_3HSe_2O_7F_2$; but the cæsium and sodium salts could not be obtained.

In 1859, R. Weber[2] prepared **selenyl dichloride,** or **selenium oxydichloride,**

$SeOCl_2$, by the action of moist air: $SeCl_4+H_2O=2HCl+SeOCl_2$, or of selenious acid, on selenium tetrachloride, and F. Clausnizer recommended heating a mixture of selenium dioxide and tetrachloride in a sealed tube for some hours at 200°; the oxydichloride can be distilled from the small excess of selenium dioxide employed. V. Lenher obtained it by adding the calculated amount of selenium dioxide to selenium tetrachloride suspended in carbon tetrachloride—or in chloroform, or selenium oxychloride itself. Reaction takes place with formation of selenium oxychloride, which dissolves in the carbon tetrachloride. The liquid can then be distilled. Carbon tetrachloride distils at 76°–77° and selenium oxychloride at 176·4°, hence they can be readily separated by distillation. Selenium oxychloride can be conveniently distilled under diminished press. to a high degree of purity; V. Lenher also prepared it by the dehydration of the complex $SeO_2.2HCl$, say, by heating a mixture of 4 parts of $SeO_2.2HCl$, and one part of sulphuric acid of sp. gr. 1·84; or selenium dioxide can be treated with hydrogen chloride, the resulting liquid mixed with excess of the dehydrating agent and the oxychloride distilled off, or selenium dioxide can be first mixed with the dehydrating agent, and this mixture treated with hydrogen chloride. C. A. Cameron and J. Macallan made it by the action of selenium dioxide on sodium chloride; and A. Michaelis, by heating a mixture of selenium dioxide and phosphoryl chloride. G. J. Fink and E. D. Giauque, and the Hooker Electrochemical Co. purified the oxydichloride by distillation in a current of chlorine.

W. J. R. Henley and S. Sugden found the mol. wt. in benzene is 195·7—theory for $SeCOl_2$ gives 166·1; and they favoured the formula $Se(OH)_2Cl_2$ for the *monohydrate*. R. Weber described selenium oxydichloride as a yellowish liquid, but V. Lenher said that by distillation under reduced press., and crystallization by freezing, a nearly colourless liquid can be obtained. The **specific gravity** of the liquid is 2·44; A. Michaelis gave 2·443; and W. C. Muchlberger and V. Lenher, 2·424 at 22°. W. J. R. Henley and S. Sugden found the sp. gr. of $SeOCl_2$ to be 2·445 at 16°/4°; 2·398 at 38·5°/4°; 2·356 at 59·5°/4°; and 2·314 at 77·5°/4°, or, at $\theta°/4°$, the sp. gr.$=2·478-0·002080\theta$; and for the monohydrate, $SeOCl_2.H_2O$, 2·253 at 14·8°/4°; 2·202 at 42·3°/4°; 2·160 at 63·5°/4°; and 2·134 at 78·6°/4°, or, at $\theta°/4°$, the sp. gr.$=2·282-0·001890\theta$. They also obtained for the **surface tension,** σ, of $SeOCl_2$:

	17·0°	41·5°	62·5°	80·5°
σ . . .	48·1	45·8	43·4	41·7
D . . .	2·443	2·392	2·348	2·310
$M\sigma^{\frac{1}{4}}(D-d)$ . .	179·1	180·7	181·6	182·8

where d denotes the sp. gr. of the vapour, and M the mol. wt. For the monohydrate

	16·2°	43·1°	61·45°	77·1°	94·4°
σ . .	52·48	49·62	46·73	45·78	43·70
D . .	2·251	2·200	2·165	2·136	2·103
$M\sigma^{\frac{1}{4}}(D-d)$	220·1	222·1	222·5	224·2	225·1

The **vapour density** at 265°–290° was found by V. Lenher and co-workers to vary from 141·5 to 164·4—average 151·4. W. J. R. Henley and S. Sugden found from its effect on the f.p. of benzene that the mol. wt. is about 194—theory for $SeOCl_2$, 166·1. Hence, the compound is associated in benzene soln. R. Weber found that at 0°, the liquid freezes to colourless crystals, which have the **melting point** at 10°. V. Lenher and co-workers gave 10·8° for the f.p. of the light straw-coloured liquid, and 8·5° for the m.p. W. C. Muchlberger and V. Lenher gave 10·9° for the m.p. R. Weber gave 220° for the **boiling point**; A. Michaelis, 179·5°; F. Clausnizer, 175°–176°; J. E. Wildish, 179·4° at 745·44 mm.; W. C. Muchlberger and V. Lenher, 176°; and V. Lenher, 176·14° at 726 mm. V. Lenher and co-workers gave for the b.p. at a press., p mm., or the **vapour pressure,** p mm., at the given temp.:

p .	21	50·4	105·5	209	313	402	511	740
B.p.	84·3°	101·5°	117·0°	133·5°	146·0°	153·5°	161·8°	177·2°

The results can be represented by $\log p = 5{\cdot}8503 + 0{\cdot}000219T - 830{\cdot}9(T-178)^{-1}$, where p denotes the vap. press. at the absolute temp. $T°$. When distilled under atm. press., selenium oxydichloride decomposes slightly, since a little selenium dioxide collects in the neck of the distilling flask; the colour of the liquid in the distilling flask changes from pale straw-yellow to reddish-brown; and the b.p. increases slightly. The minor decompositions are represented $2SeOCl_2 \rightleftharpoons SeO_2 + SeCl_4$; $2SeCl_4 \rightleftharpoons Se_2Cl_2 + 3Cl_2$; $2Se_2Cl_2 \rightleftharpoons SeCl_4 + Se$; and $4SeOCl_2 \rightleftharpoons Se_2Cl_2 + 2SeO_2 + 3Cl_2$. The presence of selenium has no measurable effect on the vap. press. between 90° and 120°; selenium monochloride up to 20 per cent., none between 89° and 121°; selenium dioxide up to saturation at 20°, none between 91° and 135°; and selenium tetrachloride up to saturation at 20°, none between 89° and 130°. V. Lenher gave 1·6516 for the **index of refraction** at 20°; while the pale yellow liquid is transparent to visible light, it is so opaque to **ultra-violet light** as to be a practically perfect screen for all wave-lengths below 4050. A. P. Julien gave 2×10^{1} mhos for the **electrical conductivity** k, at 25°, and for temp., $\theta°$ between 11·8° and 64·0°, $k = k_{25} + 0{\cdot}0392\theta - 0{\cdot}943 - 0{\cdot}0002(\theta-12)^2$. V. Lenher gave $9{\cdot}6\times10^{-4}$ mhos for the conductivity between carbon electrodes at 28°. The presence of water and hydrogen chloride increases the conductivity quite markedly; chlorine gas and selenium tetrachloride produce a similar effect, but to a much smaller degree; selenium monochloride in very small amounts causes a very slight decrease in the conductance; selenium dioxide, although but slightly soluble in the reagent, decreases the conductivity in a very marked manner. An excess of selenium dioxide acted, in a selenium oxychloride soln., very much like a dehydrating agent: $2SeOCl_2 \rightleftharpoons SeO_2 + SeCl_4$. J. E. Wildish found the **dielectric constant** of the liquid to be 51 at 10° and 46·2 at 20°, so that the temp. coeff. is 1·04 per cent. The solid has a dielectric constant of 16·8 at 0°.

V. Lenher said that the same precautions are needed in handling selenium oxydichloride as are required for other corrosive liquids. The vapours have no other physiological action than that of the hydrochloric acid produced by the hydrolysis of the oxydichloride by the mucous membrane. A. F. O. Getman discussed the relations as a solvent. V. Lenher found that **calcium hydride** is peptized by selenium oxydichloride to a gel. When the two are brought together, magnesium carbonate goes at once into the colloidal form, which state is even more accentuated when the two are boiled together. When a little water is added to the suspended gel. hydrolysis of the selenium oxydichloride is effected, and brisk effervescence at once takes place. R. Weber found that selenium oxydichloride is decomposed by **water** into hydrochloric and selenious acids. As just indicated, a small proportion of moisture raises the electrical conductivity enormously, possibly forming a complex in the liquid $SeOCl_2 + H_2O = SeO_2.2HCl$. The presence of a trace of moisture in the liquid changes the pink colour of anhydrous cobalt carbonate to blue. V. Lenher observed that the oxydichloride dissolves **bromine,** forming a reddish-brown soln., while **iodine** forms a purple soln. A. P. Julien found that **hydrogen chloride** raised the electrical conductivity owing, as in the case of moisture, to the formation of the same complex: $2SeOCl_2 + 2HCl = SeCl_4 + SeO_2.2HCl$—and selenium tetrachloride has little effect on the conductivity; the result is due to the presence of $SeO_2.2HCl$. V. Lenher showed that **potassium chloride** dissolves in selenium oxydichloride, and the soln. gives off chlorine when it is warmed; **potassium perchlorate** does not react; when **iodic acid,** or **iodine pentoxide,** is brought in contact with the oxydichloride, chlorine, and iodine chloride are formed; and a similar result was obtained with **potassium iodate,** and with **potassium periodate;** whilst **potassium bromate** first gives chlorine and then a mixture of chlorine and bromine.

The members of the **sulphur** family readily dissolve in cold selenium oxydichloride, and with sulphur, selenium monochloride, sulphur monochloride, and sulphur dioxide are formed. Dry **hydrogen sulphide** first gives a brown coloration, hydrogen chloride is then given off, and yellow selenium sulphide is formed—

which dissociates into sulphur and red selenium owing to the heat evolved by the reaction; liquid **hydrogen disulphide** reacts vigorously in the cold, forming sulphur similar products and to those obtained with hydrogen sulphide. While dry sulphur dioxide is without action even at the b.p. of the oxydichloride, if a trace of moisture be present, selenium is deposited; **sulphur trioxide** dissolves in selenium oxychloride to form a thick, heavy soln., which is a powerful solvent. This soln. will dissolve the oxides of aluminium, chromium, the rare earths, titanium, columbium, molybdenum, vanadium, and uranium, but will not dissolve the oxides of zirconium or of tungsten, and dissolves the oxide of tantalum only very slightly. When the oxydichloride is warmed with **potassium persulphate,** chlorine is evolved—with persulphate and sulphuric acid chlorine is given off with effervescence in the cold. A. Michaelis symbolized the reaction with **thionyl chloride:** $SeOCl_2+SOCl_2=SeCl_4+SO_2$. V. Lenher observed that **selenium** behaves like sulphur, while solid anhydrous **selenic acid** evolves chlorine when gently warmed with the oxydichloride; **selenium dioxide** dissolves in the liquid oxydichloride; **selenium monochloride** dissolves in the oxydichloride to the extent of 20 per cent.; **selenium tetrachloride** dissolves in the liquid—*vide supra*, vap. press. of the oxydichloride. The action with **tellurium** resembles that with sulphur and tellurium tetrachloride is formed; **tellurium dioxide** is dissolved, and when the solvent is evaporated, tellurium dioxide remains chemically unchanged; **telluric acid** behaves like selenic acid; and **tellurium trioxide** is not acted upon.

According to A. Michaelis, when **ammonia** is passed into cold selenium oxydichloride very little action occurs at first; as the mixture is heated, there is formed a dark red mass with the evolution of nitrogen: $6SeOCl_2+16NH_3=3Se+3SeO_2+12NH_4Cl+2N_2$. W. Strecker and L. Claus observed that with liquid ammonia in the presence of ether, **selenium tetramminoxydichloride,** $SeOCl_2.4NH_3$, is formed; it is decomposed by water into selenium, selenium nitride, ammonium chloride and selenite, and selenious acid. In a sealed tube, a fairly good yield of selenium nitride is obtained. V. Lenher reported that red **phosphorus** reacts in the cold with the oxydichloride, evolving light and heat, while white phosphorus reacts explosively. When the reaction occurs in an evacuated flask, cooled by ice, and with the oxydichloride in excess, phosphorus pentoxide and selenium mono- and tetra-chlorides are formed. A. Michaelis represented the vigorous reaction which occurs with **phosphorus trichloride** by the equation: $3SeOCl_2+3PCl_3=SeCl_4+Se_2Cl_2+3POCl_3$. This was verified by V. Lenher; but while A. Michaelis said that with **phosphoryl chloride**, selenium tetrachloride and phosphorus pentoxide are formed, V. Lenher observed that the two liquids are completely miscible and no selenium tetrachloride is formed. He also found that **phosphorus pentachloride** forms insoluble selenium tetrachloride and phosphoryl chloride. There is no reaction with **calcium phosphide** in the cold, but the boiling soln. reacts slowly. Liquid selenium oxydichloride slowly attacks **arsenic;** powdered **antimony** takes fire when introduced into the liquid; **bismuth** is readily attacked; **arsenic trioxide** dissolves and is acted on chemically; **arsenic and antimony sulphides** react in the cold with the liberation of heat. C. R. Wise found that selenium oxydichloride is miscible in all proportions of **arsenic trichloride;** while it dissolves 38·64 per cent. of **antimony pentachloride.** R. Weber prepared a white crystalline compound, **antimony selenium dioxyenneachloride,** $SbCl_5.2SeOCl_2$.

According to V. Lenher, **boron, silicon,** and all the various forms of **carbon**—whether graphite, charcoal, activated carbon, or diamond—are not attacked by selenium oxydichloride in the cold, and even when heated to moderate temp. At or above a red-heat, when a considerable dissociation of the oxydichloride occurs, both amorphous and graphitic carbon are oxidized. When natural coals are brought in contact with selenium oxydichloride, it reacts with the bituminous and resinic materials, extracting at least a part of these materials, leaving behind a carbonaceous residue. Thoroughly ignited coke loses nothing when treated with selenium oxychloride; partially coked soft coal does. Anthracite coal containing practically no volatile combustible matter shows little action. Semi-anthracite coals lose a considerable amount of extractive matter with selenium oxychloride, while cannel, and the bituminous coals, lose a large amount of extractive matter. The insoluble material was found to contain selenium and chlorine in considerable quantities. When the soft coals are powdered, selenium oxychloride reacts with them, evolving considerable heat. Lampblack, when treated with selenium oxychloride, loses its hydrocarbon content, leaving behind carbon. The carbonaceous matter extracted from iron and steel by treatment with a soln. of cuprous chloride gives a black extract. In the cold there is no reaction with **calcium carbide,** but there is a slow reaction on boiling. V. Lenher showed that the sat. **aliphatic hydrocarbons** are slowly attacked by selenium oxydichloride at a high temp.; while the **aromatic hydrocarbons** –like benzene and toluene—form physical mixtures which can be separated by purely physical means, such as fractional distillation. The complete recovery of the hydrocarbon can also be accomplished by hydrolysis of the selenium oxychloride with water. V. Lenher, and C. E. Frick observed that the unsaturated aliphatic hydrocarbons, or the **olefines**—like ethylene, propylene, butylene, and amylene—react more or less violently, forming the dichlorides of the corresponding alkyl selenides, regardless of whether the olefine or the oxydichloride is in excess. It is thus possible to separate such unsaturated aliphatic hydrocarbons as amylene from heptane, a sat. hydrocarbon, by simple contact with this solvent. Similarly, when a mixture of heptane and benzene is treated with selenium oxychloride the benzene forms a soln. with the selenium oxychloride, while the lighter heptane rises to the top and forms an immiscible layer. The reaction with **turpentine** is as violent as is that of the halogens on turpentine. A. Müller studied the action of selenium oxydichloride on unsaturated hydrocarbons and ketones. According to V. Lenher, natural **resins, bitumens,** and **asphalts** dissolve with ease in selenium oxydichloride in the cold when they are of unsaturated character. Such a natural product as ozocerite, which consists essentially of sat. hydrocarbons, behaves towards selenium oxydichloride much like paraffin. It is scarcely acted on in the cold, but when the two are heated together it forms a homogeneous liquid phase, which, in cooling, separates into the solid phase of hydrocarbons and the liquid phase of selenium oxydichloride. W. Strecker and A. Willing observed its action on organic magnesium compounds. V. Lenher observed that **carbon tetrachloride** is an excellent solvent for selenium oxychloride, as has been noted, but in time they react, producing selenium tetrachloride and phosgene. This is particularly true when the two are heated together for some hours. C. Chabrié and co-workers studied the action of selenium oxydichloride on **polyhydric alcohols**—erythritol, and mannitol; and A. Müller, the action on unsaturated hydrocarbons and ketones, resulting in the formation of addition products. V. Lenher found that **proteins** –like gliadin from wheat, zein from corn, glutenin from wheat, and elastin, as well as albumen, from egg and from blood—have been found to be readily attacked and dissolved by selenium oxychloride. Selenium oxydichloride dissolves hair, bristles, silk, and leather in the cold, and the action is much accelerated by heating. The oxydichloride has no appreciable action on **cellulose.** A piece of filter-paper, sealed up in a tube with selenium oxychloride, showed practically no action after being allowed to stand for 6 months. It has frequently been found convenient to filter selenium oxydichloride soln. through ordinary filter-paper during laboratory experiments. **Starch** and **cane sugar** are not appreciably acted on by selenium oxychloride in the cold, but when slightly warm, decomposition begins. The action of selenium oxydichloride with **hydrocellulose** is very sluggish, even when the two are boiled together. The behaviour of selenium oxydichloride towards **fish and vegetable oils** was found by V. Lenher to be in many respects similar to that of sulphur monochloride on the oils. With linseed oil, selenium oxychloride forms a rubber-like mass similar in many respects to that formed by sulphur monochloride. Menhaden oil reacts with selenium oxychloride to form a water rubber-like mass. The insoluble phenolic condensation products, redmanol, bakelite and condensite, dissolve with ease in selenium oxydichloride. The reaction is accelerated by heating. Chemical change takes place. Gums, resins, dried paints, shellac, dried varnish, lacquer, agar, celluloid, gelatin, glue, including the insoluble casein glues, are all dissolved readily in the cold by selenium oxydichloride. Pure **rubber,** vulcanized rubber, and vulcanite react chemically with selenium oxychloride in the cold. The reaction is much accelerated by heating. The chemical character of the rubber is changed by the reaction. The soln. obtained when hydrolyzed by water gives in addition to hydrochloric acid, selenious acid, and red selenium, a white insoluble product of gelatinous character which contains selenium and chlorine in addition to carbonaceous matter. C. E. Frick added that in the behaviour of selenium oxydichloride there is no difference in empirical composition between pure rubber hydrocarbon from the Hevea tree and the synthetic rubber made by polymerizing isoprene with metallic sodium.

V. Lenher and co-workers showed that most **metals** react with selenium oxydichloride, forming the metal chloride, and selenium monochloride; and this, in contact with water, gives hydrochloric and selenious acids, and red selenium. When **sodium** is introduced into the liquid, it is not acted on. Indeed, selenium oxydichloride can be distilled in the presence of metallic sodium and no action is apparent, even at a temp. of 176·4°, the b.p. of selenium oxydichloride. Sodium, when dropped on selenium oxydichloride, floats, and if a few drops of water be carefully added, the water will float on the heavier selenium oxydichloride. The sodium will float on top of this water, and gives off hydrogen in its usual manner without any violence. On the other hand, when **potassium** is brought in contact with selenium oxydichloride in the cold, a violent explosion occurs. W. L. Ray said that at room temp. sheet **copper** forms a film of cuprous and cupric selenides, and the black coating then changes to cupric chloride: $3Cu+4SeOCl_2=3CuCl_2+2SeO_2+Se_2Cl_2$; and **copper selenide** gives the same end-products; while cupric selenite reacts: $CuSeO_3.2H_2O+3SeOCl_2=CuCl_2+4SeO_2+4HCl$. There is a slow reaction with **silver,** which proceeds similarly to that with copper, but the film of silver selenide after it has been converted to the chloride forms a coherent film which retards further action. Precipitated silver is rapidly changed into silver chloride when carefully added to cold selenium oxychloride. Silver leaf added to cold selenium oxydichloride turns black at once, and in less than a minute is changed into a sheet of gelatinous silver chloride that floats on top of the selenium oxydichloride. If the selenium oxydichloride be hot, the reaction is similar, except that the film of silver chloride is thicker. There is a slow formation of silver chloride when the oxydichloride acts on **silver selenide.** V. Lenher found that **gold** is slowly attacked, and a similar remark applies to **calcium,** and **magnesium ;** while **zinc** is rapidly attacked. W. L. Ray observed that when **tin** is added to cold selenium oxydichloride, action begins at once. The selenium oxydichloride becomes dark red from the selenium monochloride formed during the reaction. No precipitate is formed. When sufficient tin is present, the reaction continues until the soln. becomes so viscous that it will not run from one end of the tube to the other. The tin is oxidized to stannic chloride. It was not possible to prepare R. Weber's $SnCl_4.2SeOCl_2$ from the action of selenium oxydichloride on tin. The presence of selenium dioxide and selenium monochloride dissolved in selenium oxydichloride evidently prevents the reaction between the latter and stannic chloride to form $SnCl_4.2SeOCl_2$. The reaction with **lead** is more rapid than with either copper or silver. There is no indication that lead selenide is formed as an intermediate compound. The lead chloride that is formed is granular and drops away from the metal, thus exposing fresh surfaces to the action of the selenium oxydichloride. V. Lenher found that **titanium** was unaffected after 12 months' contact with selenium oxydichloride at ordinary temp. in a sealed tube. When the two are heated to 375° for 2 hrs., the action is not appreciable; no corrosion occurred with **tantalum** at 105°–110° in 6 months' time. At 200° there was no loss of weight in 2 hrs., and at 375°, only 0·65 per cent. loss in 2 hrs.; **chromium** is readily attacked by the oxydichloride; **tungsten** wire heated with selenium oxydichloride in a sealed tube to 105° shows no tarnish until after 28 days, and there is no appreciable change in weight at 105° until after 46 days. At higher temp., 140°–200°, a week of time is required for the development of the black tarnish, while at 375°, about 10 per cent. corrosion occurred in 2 hrs. According to W. L. Ray, iron dissolves rapidly in hot selenium oxydichloride. The ferric chloride formed during the reaction remains in soln., but some of it is precipitated when the soln. in repeatedly heated and cooled. In the cold, the reaction is slow and most of the ferric chloride separates from soln. as fast as formed. There is a very slow reaction with **cobalt.** When a sheet of the metal is placed with selenium oxydichloride in a sealed tube and allowed to remain at room temp. for over a year, the selenium oxydichloride was slightly darkened by selenium monochloride, while a small amount of the metallic chloride was in the bottom of the tube. The reaction between selenium oxydichloride and the finely divided metal is more rapid. It was found that **nickel** behaves similarly; and V. Lenher added that **platinum** is slowly attacked.

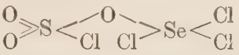
W. L. Ray observed that **cupric oxide** slowly reacts with selenium oxydichloride, $CuO+SeOCl_2=CuCl_2+SeO$; and when **cuprous oxide** is heated with the oxydichloride, cupric chloride is formed, and a little oxydichloride is reduced to the monochloride; the reaction with **silver oxide** is attended by the evolution of light and heat, forming selenium dioxide and silver chloride; and the heat of the reaction decomposes a part of the silver oxide. V. Lenher observed that **alumina, thoria, the rare earths,** and the **oxides of titanium, zirconium, columbium, and tantalum** are not appreciably attacked by the cold oxydichloride; **vanadium pentoxide** is attacked chemically. W. L. Ray observed that when a small proportion of the oxydichloride is added to lead monoxide, red-lead, or lead dioxide, the reaction is accompanied by the evolution of heat and light. With the last two oxides chlorine is evolved. The following equation represents the action of selenium oxychloride on lead dioxide: $PbO_2+2SeOCl_2=PbCl_2+2SeO_2+Cl_2$. V. Lenher observed that **chromium trioxide,** or **potassium dichromate,** dissolves in the oxydichloride to form a beautiful red soln. which, when heated, gives off fumes of chromyl chloride. When **molybdenum trioxide** has been freshly ignited, it dissolves only slightly in selenium oxydichloride, but when slightly hydrated, it dissolves readily in the reagent. The soln. of molybdenum trioxide in selenium oxydichloride, when exposed to sunlight or to strong artificial light, as, for example, from an electric arc, shows a striking reversible photochemical reaction. The soln. in a strong light becomes indigo-blue in a few minutes, and when brought into subdued light, this colour fades in a few hours to the pale yellow of the original soln. This discharge of colour can also be accomplished by heating the blue soln. to a moderate temp. There is a slow reaction between **uranium oxide** and the oxydichloride; and with **potassium permanganate,** on first contact there is no action, or at most only a superficial action, and it is only after many hours of contact that there is any appreciable reaction between the two. W. L. Ray observed that **ferric oxide** is only slowly affected by selenium oxydichloride at room temp., but when selenium oxydichloride in the vapour state is passed over ferric oxide heated to 400°, the reaction is rapid. Ferric chloride and selenium dioxide collect on the cooler portions of the tube. The reaction with **cobalt oxide** is slow, and cobalt chloride and selenium dioxide are formed; similarly also with **nickel oxide.** V. Lenher found that **cadmium sulphide** reacts in the cold with the liberation of heat; **pyrite, marcasite,** and **arsenopyrite** are slowly acted on in the cold by selenium oxydichloride, but when heated the reaction is more energetic. Sulphur dioxide is evolved and selenium monochloride is formed at the same time.

Anhydrous **sodium and potassium carbonates and hydrocarbonates** react with selenium oxydichloride giving off carbon dioxide; **copper carbonate** is only slightly attacked in the cold; **calcium carbonate** is covered with a white crust of selenite;

strontium carbonate gives off carbon dioxide, and the other products of the reaction pass into soln.; **barium carbonate** effervesces and forms an insoluble gel; and **magnesium carbonate** is peptized by selenium oxydichloride to a gel. When the two are brought together, magnesium carbonate goes at once into the colloidal form, which state is even more accentuated when the two are boiled together. When a little water is added to the suspended gel, hydrolysis of the selenium oxydichloride is effected, and brisk effervescence at once takes place. Selenium oxydichloride quickly dissolves **zinc carbonate** in the cold; **lead carbonate** is only slightly attacked; **cobalt carbonate** also is only slightly attacked—when the pink carbonate is treated with selenium oxydichloride, it instantly turns blue without showing effervescence. If water be added, the selenium oxydichloride is at once hydrolyzed, and the acid set free reacts energetically on the carbonate, causing effervescence and the formation of a blue cobalt soln., which with further addition of water transforms to the rose colour, characteristic of dil. cobalt soln. Cold selenium oxydichloride has only a slight action on **nickel carbonate.** Finely divided **barium sulphate** is peptized by contact with selenium oxydichloride, and its physical appearance is changed from the finely divided condition to that of a gel much resembling freshly precipitated aluminium hydroxide. This gelatinous form of barium sulphate can also be produced when a soln. of selenium oxydichloride containing dissolved barium chloride is treated with a soln. of selenium oxydichloride containing sulphuric acid. When these two soln. are brought together, barium sulphate is precipitated in a gelatinous form. This colloidal form of barium sulphate immediately changes to the ordinary form when treated with water.

C. R. Wise found that, at 25°, selenium oxydichloride dissolves 3·21 per cent. of **lithium chloride;** and 0·57 per cent. of **sodium chloride,** but no complex salt has been obtained; it dissolves 2·89 per cent. of **potassium chloride,** and it forms the complex salt **potassium selenium oxytrichloride,** $KCl.SeOCl_2$. The compound is hydrolyzed by water. It is soluble in alcohol, while chloroform gradually extracts the selenium oxydichloride, leaving potassium chloride. The oxydichloride dissolves 3·56 per cent. of **rubidium chloride,** forming tabular crystals of **rubidium selenium oxytrichloride,** $RbCl.SeOCl_2$; this appears as a solid phase which requires considerable time for equilibrium, followed by the separation of well-defined crystal plates accompanied by a little yellow powder. The salt is hydrolyzed by water, and is insoluble in chloroform. The oxydichloride dissolves 3·83 per cent. of **cæsium chloride,** producing a yellow, gelatinous mass which has not yet been converted into a definite compound. The oxydichloride does not dissolve anhydrous **cuprous chloride,** or **silver chloride,** and no complex salts are formed. The oxydichloride dissolves 6·11 per cent. of **calcium chloride,** forming more gelatinous products than is the case with the alkali chlorides; the complex **calcium selenium trioxyoctochloride,** $CoCl_2.3SeOCl_2$, and possibly others, are formed. The oxydichloride dissolves 5·17 per cent. of **strontium chloride,** and 3·95 per cent. of **barium chloride**—if 0·0625, 0·25, and 1·0 mol of water be present per mol of selenium oxydichloride, 3·86, 2·32, and 0·45 per cent. of barium chloride is dissolved. The oxydichloride dissolves 4·96 per cent. of **magnesium chloride,** and its action resembles that of calcium chloride, forming **magnesium selenium trioxyoctochloride,** $MgCl_2.3SeOCl_2$. The oxydichloride dissolves 1·10 per cent. of **zinc chloride,** 0·15 per cent. of **cadmium chloride,** and 0·89 per cent. of **mercuric chloride,** but forms no definite compounds; it dissolves 0·75 per cent. of **titanium tetrachloride,** and, as shown by R. Weber, it forms white crystals of the complex **titanium selenium dioxyoctochloride,** $TiCl_4.2SeOCl_2$; it dissolves 13·75 per cent. of **stannic chloride,** and R. Weber obtained white crystals of **stannic selenium dioxyoctochloride,** $SnCl_4.2SeOCl_2$. The oxydichloride does not dissolve or form a compound with **lead chloride;** and similarly with **chromium trichloride,** it dissolves 0·16 per cent. of **manganese chloride,** and 23·40 per cent. of **ferric chloride.** In the latter case the action is slow and there is a great tendency to supersaturation. Ruby-red crystals of **ferric selenium dioxyheptachloride,** $FeCl_3.2SeOCl_2$, are formed either when the selenium oxydichloride is in excess or when the ferric chloride is in excess. The compound dissolves readily in alcohol, ether, xylene, chloroform, and carbon tetrachloride. Water causes hydrolysis of the compound with the production of a yellow precipitate. The oxydichloride dissolves 0·15 per cent. of **nickelous chloride** and 0·17 of **cobaltous chloride** without forming compounds. According to V. Lenher and H. G. Taylor, when shaken with a mixture of selenium oxydichloride and heptane, **barium sulphate** passes into the oxydichloride layer; with a mixture of selenium oxydichloride and 70 per cent. sulphuric acid, it goes into the acid layer, whilst with heptane and water it remains at the interface and emulsions are readily formed. Hence barium sulphate is wetted more easily by selenium oxydichloride than by heptane, and still more easily by 70 per cent. sulphuric acid. Selenium oxydichloride has no action on barium sulphate, and the gelatinous product obtained when barium sulphate is precipitated in this solvent can therefore contain nothing but adsorbed oxydichloride. A. V. Slater studied the peptization of barium sulphate and of magnesium carbonate by selenyl chloride.

W. Prandtl and P. Borinsky[3] prepared **sulphoselenium enneaoxyoctochloride,** $2SeCl_4.3SO_3$, by melting at 140°, by the action of sulphur trioxide on selenium tetrachloride: when heated in vacuo at 155° it forms **sulphoselenium trioxytetrachloride,** $SSeO_3Cl_4$, melting at 163° and boiling at 185°. The latter can be represented by the formula:



$$\begin{matrix}O\\O\end{matrix}\!\!>S<\begin{matrix}\diagup O\diagdown\\Cl\quad Cl\end{matrix}>Se<\!\!\begin{matrix}Cl\\Cl\end{matrix}$$

It is also obtained by the action of pyrosulphuryl chloride on selenium; or of chlorosulphonic acid on selenium tetrachloride. It reacts with ammonia like selenium tetrachloride. They also obtained **sulphoselenium trioxytetrabromide,** $SSeO_3Br_4$, in an analogous way; **sulphoselenium tetroxydibromide,** $SeOBr_2.SO_3$, by the action of sulphur trioxide on selenium tetrabromide. J. Meyer and V. Stateczny could not prepare **selenium dioxydichloride,** or **selenyl chloride,** SeO_2Cl_2, analogous to sulphuryl chloride; nor could **selenochromyl chloride,** $SeCrO_5Cl_2$, analogous to $SCrO_5Cl_2$, or to $Cr_2O_5Cl_2$, be obtained—*vide supra,* chromium chloroselenates.

R. Schneider[4] melted a mixture of selenium tetrabromide and dioxide and obtained a brown liquid which solidified to needle-like crystals which probably consist of **selenium oxydibromide,** $SeOBr_2$, or **selenyl bromide.** R. T. Glauser said that when a selenium oxydichloride is distilled with sodium bromide, a dark red liquid is obtained which solidifies into a mass of yellow needles. It is also produced by the action of selenium tetrabromide on the dioxide.

V. Lenher prepared the oxydibromide by adding to sublimed selenium dioxide the calculated amount of fused selenium in a flask fitted with a rubber stopper through which passed a dropping funnel and a safety tube filled with fused calcium bromide. The flask was cooled to 0°, and the amount of bromine necessary to convert the metal into tetrabromide cautiously added in small quantities. The mixture was then warmed until the whole of the oxide had dissolved to form the oxydibromide. Selenium oxydibromide is a reddish-yellow solid of **specific gravity** 3·38 at 50°; its **melting point** is 41·5° to 41·7°—R. T. Glauser gave 30°–40°—and its **boiling point,** 217° at 740 mm. It decomposes so readily when heated that it cannot be purified by distillation even under reduced press. Its **electrical conductivity** is 60×10^{-5} ohms at 40°–50°. Selenium oxydibromide is a very active chemical reagent. If dry **air** is bubbled through the oxydibromide at 60°, bromine is set free owing to the primary dissociation of the compound into selenium dioxide and tetrabromide, followed by the secondary dissociation of the tetrabromide into monobromide and bromine. It is slowly converted by **water** into selenious and hydrobromic acids; **chlorine** displaces the bromine from the oxydibromide, and **iodine** is freely soluble in it; **sulphur** reacts readily in the cold evolving sulphur dioxide; **hydrogen sulphide** causes a slight decomposition; **sulphur dioxide** has no action on the oxydibromide; R. T. Glauser said that the oxydibromide dissolves in **sulphuric acid,** and may be largely recovered by adding a small proportion of water. V. Lenher observed that **selenium** dissolves in it, forming the monobromide; yellow **phosphorus** explodes with the solid, while red phosphorus takes fire and burns; **arsenic** and **antimony** are attacked, forming the metal tribromide and selenium monobromide; **carbon** and **silicon** are not attacked; carbon monoxide has no action; it dissolves in **carbon disulphide, chloroform, benzene, toluene,** and **xylene,** and the fused oxydibromide is miscible in all proportions with these solvents; **carbon tetrachloride** dissolves the oxydibromide readily, but the fused material dissolves only to the extent of 6 per cent., and on heating the soln. for several days, carbonyl chloride and selenium tetrachloride are formed. The oxydibromide reacts explosively with **sodium,** producing the bromide and selenium monobromide, whilst **potassium** reacts even more violently; **mercury, tin, bismuth, iron, calcium, copper, lead, silver, molybdenum, thallium, gold, platinum,** and **zinc** are all attacked, forming the metallic bromide and selenium monobromide. Zinc dust burns in the oxybromide; **aluminium** and **magnesium** are only slightly corroded after heating for a week at 100° in the oxybromide. **Calcium, chromium, nickel, cobalt, tungsten,** and **tantalum** are not attacked when heated for ten days at 100°. The **oxides of mercury, silver, calcium, and sodium** react energetically with selenium oxybromide, the **oxides of arsenic, tin, and tellurium** less energetically, and the **oxides of columbium, tantalum, vanadium, thorium, titanium, zirconium, and uranium** are unattacked after heating for several days at 100°. With most **carbonates,** the anhydrous oxybromide reacts only sluggishly even on heating, but in the presence of moisture the reaction is vigorous. The commoner **sulphides** react with the oxybromide with the development of heat, forming metallic bromides and selenium monobromide. **Potassium chlorate** liberates bromine from the oxybromide, but **potassium perchlorate, permanganate, dichromate, and chromium trioxide** are without action on it.

R. R. le Geyt Worsley and H. B. Baker [5] found that considerable heat is evolved by the combination of hydrogen chloride and selenium trioxide and partial decomposition occurs, red selenium being formed. If, however, the temp. be kept down by immersing the reaction vessel in ice, no decomposition takes place and a nearly colourless liquid is formed. Analysis agrees with **chloroselenic acid,** $HClSeO_3$; and the mol. wt. determined from the lowering of the f.p. of soln. in phosphoryl chloride agrees with the doubled formula $(HClSeO_3)_2$. Chloroselenic acid obtained is a nearly colourless liquid which slowly turns pale yellow. It fumes in the air, evolving hydrogen chloride. Its density is 2·26 and it solidifies at —46°. On heating, it is decomposed, evolving hydrogen chloride and leaving selenium dioxide and selenium. The chloroselenic acid dissolves very readily in water, evolving considerable heat, and forming selenic and hydrochloric acids. It is also decomposed by alcohol, heat being evolved and selenium precipitated. It is insoluble in ether, benzene, chloroform, or carbon tetrachloride, but dissolves readily in selenium oxydichloride without decomposition.

A. Ditte observed that hydrogen fluoride is copiously absorbed by selenium dioxide; and E. B. R. Prideaux and J. O'Neil Millott froze out from the accompanying liquid the complex **selenium dioxypentahydrofluoride,** $SeO_2.5HF$, a rare example of a combination of hydrogen fluoride with an acid anhydride. The compound is in equilibrium with liquids of various compositions. It dissociates in the vapour phase, giving off small quantities of hydrogen fluoride, the vap. press. of which is only a small fraction of that of the pure acid. At higher vap. press., the dissociation of the vapour which contains selenium dioxide is not complete. Thus, the same compound is obtained either by distillation of the excess of hydrogen fluoride or by freezing from liquids of different compositions. According to A. Ditte, selenium dioxide absorbs dry hydrogen chloride with the development of much heat to form acicular crystals which disappear as the temp. rises to 20°. The liquid has the composition $SeO_2.2HCl$. V. Lenher obtained it by passing hydrogen chloride over silver selenite: $Ag_2SeO_3+4HCl=2AgCl+H_2O+SeO_2.2HCl$. A. Ditte said that the compound loses hydrogen chloride as the temp. rises above 26°. The dissociation press., p mm., is:

	10°	30°	40°	55°	75°	100°	118°
p . . .	0	15	48	142	313	664	1012

V. Lenher found that the product easily loses water, giving the oxydichloride. C. W. Muehlberger and V. Lenher inferred that the complex $SeO_2.2HCl$ is really *hydrated* selenium oxydichloride, $SeOCl_2.H_2O$, with a sp. gr. 2·246 at 25°; a surface tension of 55 dynes per cm. at 25°; a m.p. below 100°; an index of refraction of 1·642 at 20°; and an electrical conductivity of $2·7\times10^{-2}$ mho. Dissociation begins at 94°, and the b.p. rises to 179° without any indication of the formation of a constant boiling mixture. A. Ditte also prepared $SeO_2.4HCl$, in needle-like crystals, by the action of dry hydrogen chloride on the preceding salt. It is decomposed by heat, and it is best made at a temp. of −10° to −15°. At −30°, the dissociation press., p mm., is zero; and

	−20°	−18°	0°	12°	15°	25°	33°
p . . .	60	70	219	418	483	760	995

The salt dissolves in water with the evolution of a little gas. T. W. Parker and P. L. Robinson, and G. F. Hoffmann and V. Lenher obtained **selenium dioxydihydrochloride,** $SeO_2.2HCl$, and **selenium dioxytetrahydrochloride,** $SeO_2.4HCl$, by the action of hydrogen chloride on selenium dioxide. The first is a yellow liquid, stable up at 170°, and able to be distilled at this temp. with some decomposition; the second compound is a yellow solid, stable at 0°. A. Ditte found that hydrogen bromide is also absorbed by selenium dioxide to form $SeO_2.4HBr$. The steel-grey plates exert no perceptible dissociation press. at 55°, but at higher temp. decompose into selenium, bromine, and water. It dissolves in water, forming a soln. almost black in colour. The compound absorbs hydrogen bromide at −15° to form $SeO_2.5HBr$. The brown plates decompose at 65° into bromide and water, forming the preceding salt. The compound has no perceptible dissociation press. at −25°; at −6° it is 100 mm.; at 0°, 135 mm.; at 30°, 287 mm.; at 54°, 404 mm.; and at 54°, bromine appears, indicating some decomposition as distinct from dissociation. C. W. Muehlberger and V. Lenher said that $SeO_2.2HBr$ is identical with *hydrated* **selenium oxydibromide,** $SeOBr_2.H_2O$. Its sp. gr. is 3·077 at 22°. It is obtained as a red-brown oil on passing hydrogen bromide over selenium dioxide. At 115°, it begins to decompose, producing bromine, selenium monobromide, tetrabromide, and oxybromide, selenium dioxide, water, and hydrogen bromide. On cooling to −10°, crystals of selenium tetrabromide separate. An excess of selenium dioxide causes the separation of yellow needles of the oxybromide, $SeOBr_2$, melting at 40°. They prepared $SeO_2.4HBr$, but could not obtain $SeO_2.5HBr$. A **selenium hydrodioxyiodide** is formed by the absorption of hydrogen iodide by selenium dioxide, but it decomposes at −10°, into water, iodine, and selenium.

According to W. Muthmann and J. Schäfer, when an attempt is made to prepare chloroselenates, analogous to the bromoselenates, from a soln. of selenious acid, and, say, ammonium chloride in hydrochloric acid, colourless, monoclinic crystals of **potassium chloropyroselenite,** $KSe_2O_4Cl.2H_2O$, are formed. If the soln. of potassium chloropyroselenite is treated with silver oxide, and the filtered soln. evaporated, crystals of the tetraselenite $KH_3(SeO_3)_2$ are deposited. This salt loses two-thirds of its water at 100° and is considered to be a pyroselenite, $KHS_2O_5.H_2O$, so that the potassium salt is $KO.SeO.O.SeO.Cl$. Similarly also with **ammonium chloropyroselenite,** $(NH_4)Se_2O_4Cl.2H_2O$, and **rubidium chloropyroselenite,** $RbSe_2O_4.Cl.2H_2O$. W. Muthmann and J. Schäfer also prepared **potassium bromopyroselenite,** $KSe_2O_4Br.2H_2O$; and **ammonium bromopyroselenite,** $(NH_4)Se_2O_4Br.2H_2O$. J. Meyer and H. Wilk prepared **thallosic chloroselenate,** $Tl'''Tl'Cl_2(SeO_4)$, by the reaction symbolized: $2HTl(SeO_4)_2.4H_2O+HCl=Tl'''Tl'Cl_2(SeO_4)+Cl_2+H_2SeO_4+8H_2O$; and similarly with **thallosic bromoselenate,** $Tl'''Tl'Br_2SeO_4$.

According to R. F. Weinland and G. Barttlingck,[6] **potassium selenatomonoiodate,** $2K_2O.2SeO_2.I_2O_5.H_2O$, is obtained by evaporating over sulphuric acid at ordinary temp., a soln. of selenic acid, iodic acid, and potassium hydroxide in the molar proportions 6 : 1 : 6. If less selenic acid be used, the first crop of crystals is potassium iodate, and if more, the yield is poor. If less potassium hydroxide be used, the selenatotriiodate is formed. The crystals are four-sided prisms, which are stable in air and do not effloresce over sulphuric acid. Water decomposes the salt, forming iodate. The corresponding **ammonium selenatomonoiodate,** $2(NH_4)_2O.2SeO_3.I_2O_5.H_2O$, is obtained in a similar way using 8 : 1 : 7 molar proportions of selenic acid, iodic acid, and ammonia. If the proportions 7 : 1 : 1 be employed, **ammonium selenatotriiodate,** $2(NH_4)_2O.2SeO_3.3I_2O_5.5H_2O$, is obtained in colourless prisms, similarly also with selenic acid, iodic acid, and potassium hydroxide in the proportions 6 : 1 : 3, or 6 : 1 : 1, **potassium selenatotriiodate,** $2K_2O.2SeO_3.3I_2O_5.5H_2O$, is obtained in colourless crystals which are stable in air and do not effloresce over sulphuric acid. The salt is decomposed by water. Similarly, using a soln. with selenic acid, iodic acid, and rubidium hydroxide in the molar proportions 7 : 1 : 4, **rubidium selenatotriiodate,** $2Rb_2O.2SeO_2.3I_2O_5.5H_2O$, is formed.

H. Fonzes-Diacon[7] obtained **mercuric diselenodifluoride,** $HgF_2.2HgSe$, by passing hydrogen selenide into a soln. of yellow mercuric oxide in fuming hydrofluoric acid. When dried at 110°, the precipitate is yellow. It is decomposed by alkali-lye, and by boiling water. H. Uelsmann obtained **mercuric diselenodichloride,** $HgCl_2.2HgSe$, by the action of hydrogen selenide on a soln. of mercuric chloride, and by the action of an excess of mercuric chloride on potassium selenide or a soln. of selenium in ammonium sulphite soln. The white powder, when heated, decomposes into mercuric selenide and a sublimate of mercuric chloride. Soda-lye blackens it, and when boiling, it forms an oxyselenide. It is insoluble in hydrochloric, sulphuric, and nitric acids even when boiling; it is freely soluble in aqua regia, and in a mixture of conc. sulphuric and nitric acids. H. Fonzes-Diacon also prepared **mercuric tetraselenodichloride,** $HgCl_2.4HgSe$, by the action of hydrogen selenide on a soln. of mercuric chloride mixed with a hydrochloric acid soln. of cuprous chloride—the product may be a mixture of selenium and diselenodichloride. H. Fonzes-Diacon reported **mercuric diselenodibromide,** $HgBr_2.2HgSe$, as in the case of the corresponding diselenodichloride. He also reported **mercuric tetraselenodibromide,** $HgBr_2.2HgSe_2$, like the corresponding $HgBr_2.2HgSe_2$. F. Olivari determined the f.p. of mixtures of selenium and mercuric chloride, and the resulting curve, Fig. 63, shows no sign of a chemical compound. There is a region of limited immiscibility in the liquid state for soln. with between 16 and 53 per cent. of selenium. The eutectic at 210° corresponds with 81 per cent. of selenium. H. Fonzes-Diacon also obtained **mercuric diselenodiiodide,** $HgI_2.2HgSe$, by the method used for the diselenodichloride.

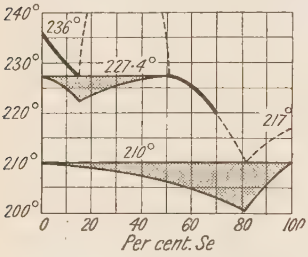


FIG. 63.—The Freezing Points of Mixtures of Mercuric Bromide and Selenium.

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§ 15. Selenium Sulphides

F. Stromeyer[1] found selenium mixed with the sulphur of the Lipari Islands, W. Haidinger called the admixture *volcanite ;* L. Bombicci, *eolide*—after the name Aolian Islands ; and J. Dana, *selensulphur*. E. Quercigh described the native selensulphur which occurs on Vulcano, Aeolian Islands, in thin adherent layers in an altered siliceous rock. The amorphous, vitreous, brownish-red mass has a conchoidal fracture ; and it is, microscopically, transparent, blood-red, isotropic, and not pleochroic. It contains minute, opaque impurities, and has a sp. gr. between 2·544 and 2·675. Traces of tellurium, and arsenic are present. J. D. Dana showed that the sulphur of Kilauea, Sandwich Islands, is seleniferous, and G. V. Brown found that an orange-red or sulphur-yellow incrustation on the slaggy lava from the crater of Kilauea contained sulphur and selenium in the at. ratio 45·5 : 1, and no tellurium. E. Divers discussed the seleniferous sulphur of Japan, which also contains some tellurium.

J. J. Berzelius found that sulphur and selenium may be fused together in all proportions ; but he seems to have assumed, partly by analogy with the oxides, that two chemical individuals are formed, namely, selenium di- and tri-sulphides—SeS_2 and SeS_3. B. Rathke made a similar observation, and A. Bettendorff and G. vom Rath stated that no crystalline compounds are formed during the freezing of the molten mixture. W. E. Ringer showed that the molten elements are miscible in all proportions, but when the proportion of selenium is greater than 10 at. per cent., crystallization does not readily occur. Even by very slow cooling, the mixture solidifies in an amorphous form ; and when the proportion of selenium is high, crystallization can be completed only by heating the selenium for many hours near its m.p. The crystalline mixtures probably contain only mixed crystals, and no evidence of the formation of a compound was observed. The following final m.p. were observed with mixtures containing the following atomic percentages of selenium which melted at 217·4°–217·8°—the m.p. of the sulphur being 118·2°–119° :

Se .	10	20	30	40	50	60	70	80	90
M.p. .	116·5°	114·2°	108°	106°	130°	136°	150°	170·5°	188°

The initial m.p. of the mixture with 10 per cent. of selenium was 114°. The whole of the results are plotted in Fig. 64. E. Beckmann and C. Platzmann found selenium to be sparingly soluble in sulphur, and with soln. up to 2·5 per cent. Se, the raising of the f.p. averaged 0·242° per one per cent. Se; and it is concluded that selenium is present as Se_3. A. Bettendorff and G. vom Rath, and W. Muthmann studied the isomorphous crystals obtained from soln. of the two elements in carbon disulphide. W. E. Ringer gave the results summarized in Fig. 65. According to W. Muthmann, one set of solid soln. takes the form of the monoclinic prisms of sulphur with $a : b : c = 1{\cdot}0609 : 1 : 0{\cdot}7094$, and $\beta = 91° \ 47'$; thus, crystals with 48 per cent. selenium had the axial ratios $a : b : c = 1{\cdot}0614 : 1 : 0{\cdot}7046$, and $\beta = 91° \ 18'$. The other set takes on the form of the monoclinic prisms of selenium with $a : b : c = 1{\cdot}6349 : 1 : 1{\cdot}6095$, and $\beta = 104° \ 2'$; thus, crystals with 68·5 per cent. selenium have $a : b : c = 1{\cdot}5925 : 1 : 1{\cdot}5567$, and $\beta = 105° \ 29'$. In the case of molten mixtures, W. E. Ringer observed three series of solid soln.: (i) solid soln. of the first type of monoclinic sulphur with 0 to 27 at. per cent. of selenium; (ii) solid soln. of the second type of monoclinic sulphur with about 50 to 82 at. per cent. of selenium; and (iii) hexagonal or (trigonal) mixed crystals of the type of the metal selenium, with 87 to 100 at. per cent. of selenium. When selenium is added to sulphur, the transition point (95·5°) from the monoclinic to the rhombic variety is lowered; when 2·05 at. per cent. of selenium is present the transition point is 93·5°; with 4·25 at. per cent. it is 91°–93°; with 7 at. per cent. it is 83°–86°, and with 12 at. per cent. it is 76°–82°. The mixed crystals of series (i), therefore, exhibit the same transition from monoclinic to rhombic crystals below a certain temp. that sulphur does. The mixed crystals of the other two series do not show any transition. At the ordinary temp. there exist a series of rhombic crystals with 0 to 10 at. per cent. of selenium, and the second (extending, however, only from 55–75 at. per cent. of selenium), and the third series just mentioned. L. Losana studied the ternary system: S–Se–Te—*vide* tellurium. M. Padoa found the at. heat of sulphur in mixtures containing 4, 9, 28·7, and 90·35 per cent. of rhombic sulphur to be respectively 7·03, 6·00, 5·87, and 5·50; and with 90·35 per cent. of monoclinic sulphur, 5·78—*vide* sp. ht. sulphur. H. E. Merwin and E. S. Larsen proposed mixtures of selenium and sulphur as immersion media in the determination of high refractive indices. They found for the indices of refraction for the Na- and Li-lines of mixtures containing the following percentages of selenium:

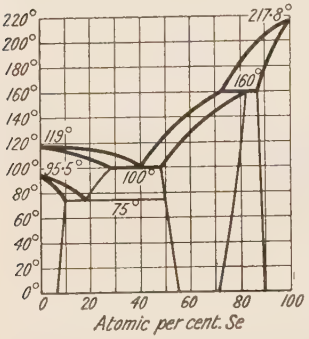

FIG. 64.—Melting Points of Mixtures of Selenium and Sulphur.

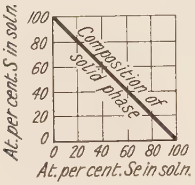

FIG. 65. — Composition of Solid Soln. of Sulphur and Selenium from a Soln. of the Two Components.

Se .	0·0	9·0	25·0	48·2	64·0	75·0	80·0	93·8	100 per cent.
μ_{Na} .	1·978	2·000	2·050	2·125	2·250	2·350	2·400	2·600	2·716
μ_{Li} .	1·998	2·022	2·078	2·163	2·307	2·423	2·490	2·755	2·920

J. J. Berzelius obtained what he regarded as **selenium disulphide,** SeS_2, by passing hydrogen sulphide into selenious acid. The lemon-yellow precipitate becomes orange-yellow and remains suspended in the liquid for a long time; but it is flocculated by warming the liquid, or by the addition of an acid. The analysis is in agreement with that required for the disulphide. The powder dries to a red colour. If the selenious acid be mixed with nitric acid, and then treated with hydrogen sulphide, E. von Gerichten found that the product has 39·0 instead of the theoretical 55·4 per cent. of selenium; and B. Rathke found that after dissolution in and crystallization from carbon disulphide, the product had 63·86 per cent. of selenium. According to E. Divers and T. Shimidzu, hydrogen sulphide passed into a cold, dil. soln. of selenious acid gives a yellow, pulverulent precipitate containing S : Se=2 : 1, *viz.* $2H_2S+H_2SeO_3=2S+Se+3H_2O$; but if the soln. is warm, another reaction sets in, forming sulphuric acid and selenium: $2H_2S+4H_2SeO_3=2H_2SO_4+4Se+4H_2O$, so that the precipitate becomes richer in selenium; dil. sulphurous acid with an excess of a conc. soln. of hydrogen selenide yields a deep red precipitate of selenium free from sulphur: $2H_2Se+H_2SO_3=2Se+S+3H_2O$; and the sulphur reacts with the excess of hydrogen selenide: $H_2Se+S=H_2S+Se$; but gaseous hydrogen selenide passed into sulphurous acid gives an orange-red precipitate containing sulphur: $6H_2Se+2H_2SO_3=6Se+2H_2S+6H_2O$. The hydrogen sulphide there reacts with the sulphurous acid in excess, $2H_2S+H_2SO_3=3S+3H_2O$. E. von Gerichten observed that if an excess of hydrogen sulphide be passed into a soln. of selenious acid in an excess of potash-lye, the liquid becomes reddish-brown, and then selenium is slowly deposited. He assumed that the selenious acid is completely reduced, forming the sulphide, which is then decomposed by the alkali-lye to form a soln. of polysulphide. If less hydrogen sulphide be introduced, and the reddish-brown soln. be treated with sulphuric acid, there is formed a mixture of selenium and sulphur approximately in the proportion Se : Se_2 is precipitated; and if a soln. of potassium selenite and sulphuric acid be treated with hydrogen sulphide, the precipitate has the composition SeS_2; while if selenious acid be mixed with ammonium sulphide, the reddish-brown precipitate of SeS_2 is formed, which is freely soluble in an excess of ammonium sulphide.

According to J. J. Berzelius, selenium disulphide softens at 100°, and melts at a slightly higher temp.; at a still higher temp. it boils and distils. When burnt in air, sulphur dioxide is the chief product, afterwards selenium dioxide, and if the supply of air be limited, some selenium sublimes unburnt. H. Rose found that chlorine gas forms a mixture of selenium and sulphur chlorides, and the latter is volatilized before the former. J. J. Berzelius said that nitric acid slowly decomposes the disulphide, while aqua regia acts quickly; when the disulphide is fused with a small proportion of potassium carbonate, the product when extracted with water leaves a residuum of selenium, whereas if a large proportion of the carbonate be employed, the whole is soluble in water; a small proportion of potash-lye extracts sulphur and leaves a residuum of selenium containing a little sulphur, whereas with a large proportion of alkali-lye, all the sulphur and a little selenium are dissolved while selenium remains as a residuum. A soln. of potassium sulphide or hydrosulphide abstracts sulphur from the disulphide, with the separation of selenium—the latter solvent only after prolonged boiling. If the solvent be in excess, some selenium is dissolved, and sulphur free selenium remains; if but a small proportion of the solvent is used, no selenium is dissolved.

According to A. Gutbier, a soln. of **colloidal selenium disulphide** is formed when hydrogen sulphide is passed into a neutralized aq. soln. of selenious acid. The yellow and green fluorescent liquid can be filtered in the usual way without change; it is slowly coagulated in the presence of electrolytes. A. Gutbier and J. Lohmann added that when the hydrosol is boiled in the presence of hydrochloric acid, a bright red precipitate is formed; and this reaction is influenced by light, heat, time, and press. The hydrosol obtained by passing hydrogen sulphide into an aq. soln. of selenium dioxide also does not contain selenium and sulphur chemically combined, since, when the soln. is repeatedly agitated with carbon disulphide, the total amount of sulphur present can be separated.

According to A. Ditte, if a very dil. soln. of selenious acid at 0° to 5° be saturated with hydrogen sulphide, a lemon-yellow powder is produced which can be well washed and dried in vacuo; it is a mixture of **selenium monosulphide,** SeS, and sulphur: $SeO_2+2H_2S=2H_2O+SeS+S$, the supernatant liquid contains neither selenium nor pentathionic acid. If the mixture be left for some time moistened with carbon disulphide, it furnishes orange-yellow scales having the composition of selenium monosulphide, for the excess of sulphur in the original precipitate goes into soln. If a neutral selenite soln. be used in place of selenious acid, the monosulphide can be more readily obtained in the subsequent treatment with carbon disulphide, but it is then of a dark reddish-brown colour, and a slightly smaller content of sulphur. E. Divers and T. Shimidzu considered that this is the only sulphide of selenium whose existence as a chemical individual has been established. A. Ditte said that during its formation there is an increase in vol., and an absorption of heat. The sp. gr. is 3·056 at 0°, and 3·035 at 52°, making the coeff. of expansion between 0° and 52°, 0·0001476; the sp. ht. is 0·1274. The monosulphide melts when heated, giving off first vapours of sulphur, and then a mixture of sulphur and selenium. It is insoluble in water and ether; and soluble in carbon disulphide, from which soln. it cannot be obtained by crystallization; it gradually blackens in contact with absolute alcohol owing to its decomposition into its constituents; and a soln. of potassium sulphide is coloured reddish-brown. According to B. W. Nordlander, paper coated with selenium sulphide is blackened on exposure to air containing traces of mercury vapour.

While J. J. Berzelius, and B. Rathke assumed that the precipitate obtained by the action of hydrogen selenide is a chemical individual, H. Rose, and E. Wohlwill regarded it as a mixture of the two elements. E. von Gerichten said that the lemon-yellow product first precipitated is a chemical compound, but it is unstable, and is soon reddened by the separation of selenium as a product of the decomposition. B. Rathke seemed to consider that owing to the similarity in the chemical mixtures of sulphur and selenium, their affinity for one another is weak, and that they can form an indefinitely large series of compounds—recalling the homologous hydrocarbons—with Se_4S as the lower limit and SeS_4 as the upper limit. He found that by the fractional crystallization of soln. of selenium sulphide in carbon disulphide, the first crop of crystals are rich in selenium, and successive fractions gradually become richer in sulphur. This variation in composition is usually taken to indicate that only mixtures, not chemical individuals, are involved. The same conclusion has been drawn from the general action of various solvents. In spite of their variable composition, B. Rathke maintained that the crystals formed by fusing together selenium and sulphur and crystallizing the product from carbon disulphide contain a definite sulphide of selenium. (i) Unlike free selenium, the product is not rendered insoluble in carbon disulphide by heating at 100°. (ii) In spite of their very great difference in solubility, selenium and sulphur cannot be separated from the product by fractional crystallization. (iii) As shown by W. E. Ringer, the solubility of selenium associated with sulphur is several times as great as that of free selenium. E. Divers and T. Shimidzu stated that the copious volatilization of sulphur which occurs when the precipitation takes place in hot soln., and the fact that in precipitating any true metal sulphide from a hot soln., no such volatilization of sulphur occurs, even in the case of tellurium sulphide, is taken as proof that the nascent sulphur is uncombined with the selenium when precipitated along with it. The selenium monosulphide alone has been established as a chemical individual. A. Gutbier and J. Lohmann studied the action of hydrogen selenide on sulphurous acid, and of hydrogen sulphide on selenious acid, and found that the orange-red product prepared by the action of hydrogen sulphide on an aq. soln. of selenious acid in the absence of air and of light contained 58·1 per cent. of selenium and 41·8 per cent. of sulphur, whilst the product obtained under press. contained 17·63 per cent. of selenium and 82·27 per cent. of sulphur, whereas SeS_2 requires Se=55·23 and S=44·77 per cent. At the ordinary temp., in the presence of air, a product is obtained which, when heated, becomes red and has the formula SeS_2; at higher temp., a product richer in selenium is obtained, and at lower temp., the product contains more sulphur than selenium. These results indicate that a compound is not formed. At the ordinary temp., hydrogen sulphide acts as a reducing agent according to the equation: $H_2SeO_3+2H_2S=Se+S_2+3H_2O$. At higher temp., the liberated sulphur is oxidized to sulphur trioxide. From the mixture obtained by the action of hydrogen sulphide on selenious acid, the sulphur can be mechanically separated by extraction with a mixture of benzene and carbon disulphide. W. E. Ringer's observations, Fig. 64, lend no support to the hypothesis that selenium sulphides are formed when mixtures of the two elements are melted together.

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§ 16. Sulphoselenides

C. Messinger[1] prepared **sodium sulphodiselenide,** $Na_2SSe_2.5H_2O$, as a mass of dark red scales, by boiling selenium with an aq. soln. of sodium hydrosulphide in a current of hydrogen, and adding alcohol to the soln. The hygroscopic salt rapidly decomposes in air, forming sodium sulphide and selenium.

E. Keller treated an acidic or ammoniacal soln. of copper and selenium with hydrogen sulphide, washed the precipitate with cold water, and digested it with a conc. soln. of sodium hydrosulphide, etc., and obtained what appeared to be **copper disulphoselenide,** $2CuS.CuSe$. The mineral *aguilarite*, previously described, is possibly **silver sulphoselenide,** $Ag_2S.Ag_2Se$. H. W. D. Wood described the use of **cadmium sulphoselenides** as pigments in painting. The mineral *onofrite*, previously described, is regarded as **mercury sulphoselenide,** $4HgS.HgSe$.

A. Stock and E. Willfroth prepared **carbon sulphoselenide,** $CSSe$, by maintaining an arc under carbon disulphide between a graphite cathode, and an anode made of graphite and selenium (17·5 : 100). The reddish-brown soln. had black particles of selenium and graphite is suspension ; and it contained non-volatile decomposition products of carbon disulphide, and carbon subsulphide, Cs_3S_2, and carbon sulphoselenide. These two compounds were separated by fractional distillation in carbon disulphide vapour, and subsequently converting the carbon subsulphide into a non-volatile complex by treatment with β-naphthylamine. The sulphoselenide was then separated by distillation. H. V. A. Briscoe and co-workers obtained some sulphoselenide by passing the vapour of carbon disulphide over ferrous selenide at 650°, and fractionating the product.

Carbon sulphoselenide is a deep yellow liquid which is stable in air. The vapour is lachrymatory, and causes violent irritation of the nasal mucous membrane ; when diluted with air, it has a pungent, onion-like odour. The liquid is oily and moderately viscid, and it wets glass only partially. The analysis agrees with $CSSe$, and H. V. A. Briscoe and co-workers found that the vapour density corresponds with this formula, so also do cryoscopic observations of the mol. wt. in benzene and in bromoform. A. Stock and E. Willfroth gave 1·979 for the sp. gr. at 20°/4° ; whilst H. V. A. Briscoe and co-workers obtained 1·9874 at 20°/4° ; 1·9777 at 25°/4° ; 1·9678 at 30°/4° ; and 1·9484 at 40°/4°. The surface tension varied from 39·70 to 40·44 dynes per cm. at 20°, so that the mol. parachor $M\gamma^{\frac{1}{4}}/D$ is 156·4, which is taken to be in accord with the formula Se=C=S. The coeff. of cubical expansion is 0·000996 between 20° and 40°. The b.p. is 83·90 to 83·95° at 749·2 mm. A. Stock and E. Willfroth gave 84° for the b.p. ; —85° for the m.p. ; 45 mm. for the vap. press. at 10° ; and $\mu=1·7379$ for the index of refraction with *D*-light at 20°.

A. Stock and E. Willfroth said that the liquid is decomposed by light, and by heat, and when kept for a long time at room temp. The decomposition products do not contain any substance corresponding with the diselenide, CSe_2. H. V. A. Briscoe and co-workers' product was probably of a higher degree of purity, since it was not decomposed if kept in the dark. Some decomposition occurred when the liquid was exposed to sunlight. The liquid furnishes hydrogen sulphide and selenide when it is reduced by nascent hydrogen from zinc and hydrochloride acid. Carbon sulphoselenide is non-inflammable, but when warmed, its vapour burns with the intense blue flame characteristic of selenium compounds. The compound is immiscible with water. Carbon sulphoselenide reacts with chlorine at ordinary temp. to form thiocarbonyl and selenium tetrachlorides ; and with bromine to form thiocarbonyl and selenium tetrabromides. If the sulphoselenide be suspended in water and treated with bromine, a thick oil is obtained ; this solidifies, and when crystallized from benzene it furnishes **carbon disulphoselenohexabromide,** $C_2S_2SeBr_6$, as a white solid with a smell recalling that of phosphorus. The solid distils under reduced press. If heated slowly, it melts sharply at 90°, but if kept at 78° it slowly liquefies. This is taken to indicate that the substance exists in two forms—one solid, one liquid. Carbon sulphoselenide dissolves sulphur very sparingly, but selenium is insoluble. At ordinary temp., hydrogen sulphide, and hydrogen selenide have no action. When the sulphoselenide is in contact with aq. ammonia for several hours at 15°, or for a few minutes at 80°, a yellow solid is produced which is insoluble in all solvents tried, but it forms a blood-red soln. with boiling aq. ammonia. The soln. deposited an orange-red, gelatinous mass when it was acidified. Carbon sulphoselenide is decomposed by heat. The action of gaseous ammonia on a soln. of the sulphoselenide in absolute alcohol is attended by a considerable rise of temp. and a blood-red soln. is formed from which a red amorphous precipitate is deposited. Carbon sulphoselenide reacts with phenylhydrazine in alcoholic soln. with the evolution of heat ; and the soln. slowly deposits light greenish-yellow, tabular crystals which are probably $(C_6H_5.NH.NH_2)_2CSSe$, analogous to the compound formed with carbon disulphide. Carbon sulphoselenide is freely soluble without decomposition in ethyl alcohol, bromoform, acetone, benzene, and other organic solvents. An alcoholic soln. of carbon sulphoselenide and aniline gives off hydrogen selenide and sulphide for 2 days, and deposits white crystals of $(C_6H_5.NH)_4CSSe$. Attempts to prepare compounds analogous to the thiocarbonates by the interaction of carbon sulphoselenide with aq. soln. of sodium sulphide, or ammonium polysulphide, or sodium hydroxide gave blood-red soln., from which no crystalline product could be isolated, but a gelatinous precipitate was formed when the soln. was acidified. An alcoholic soln. of sodium ethoxide was found by A. Stock and E. Willfroth to furnish **sodium monoselenoxanthate,** $SeC(SNa)(OC_3H_5)$, in deliquescent, yellow crystals. A soln. of this substance gives with the salts of the heavy metals products analogous to those produced with sodium xanthate.

J. Meyer prepared **phosphorus sulphoselenides,** believed to be P_4S_2Se, and P_4SSe, from the elements. Their m.p. are respectively 186° to 187°, and 217°. Mixtures made up of phosphorus tetratriselenide, and tetratrisulphide were found to have the same m.p., so that it is thought that the supposed compounds may be only isomorphorus mixtures.

A. Ditte prepared **potassium selenosulphostannate,** $K_2S.SnSe_2.3H_2$, by boiling a conc. soln. of potassium sulphide with the theoretical amount of selenium and a slight excess of tin, and evaporating the soln. in vacuo. It forms yellow octahedra, very soluble in water, with formation of a rose or red soln., according to the degree of conc. Both the soln. and the crystals decompose when exposed to air, a black crystalline selenium being liberated. A. Ditte also obtained **ammonium selenosulphostannate,** $(NH_4)_2S.3SnSe_2.3H_2O$, by treating an excess of hydrated tin diselenide with a conc. soln. of ammonium hydrosulphide in the cold, filtering, and evaporating the red filtrate in a vacuum over potassium hydroxide and sulphuric acid. It forms yellowish-red plates, less stable than the preceding compound. The crystals are decomposed by water, with separation of red flakes of tin diselenide.

E. von Gerichten prepared **arsenic disulphoselenide,** As_2S_2Se, by melting arsenic triselenide and trisulphide in the correct proportions. It appears as a red, transparent, perfectly homogeneous mass, with a bright, deep black fracture. It is soluble in the cold, if finely powdered, in ammonium hydrosulphide, imparting to the soln. a dark brown-red colour. If it be left to itself for a couple of days all the selenium separates; a soln. of ammonium carbonate dissolves it, with the exception of a little selenium. When the ammonium sulphide is decomposed by an acid, a reddish-yellow precipitate is obtained with 23·10 per cent. instead of 21·91, which the formula given above requires. Similarly, **arsenic sulphodiselenide,** As_2SSe_2, was obtained as a non-transparent, apparently perfectly crystalline mass, which distils unchanged, and dissolves in ammonium hydrosulphide with somewhat more difficulty than the previous compound, giving to the liquid a fine deep yellow colour, and leaving a slight residue. On standing, the soln. gradually changes to red. When decomposed by acids it gives a brown-red precipitate with about 11·01 per cent. S, instead of 9·46; and is therefore essentially different from the previous compound. According to E. Szarvasy, **arsenic disulphotriselenide,** $As_2S_2Se_3$, is formed when arsenic disulphide and selenium are heated together in the requisite proportions in an atm. of nitrogen; it is best purified by repeated distillation under low press., and then forms a black, highly glistening substance which, in thin plates, has a purple-red colour. In chemical properties it resembles arsenic pentaselenide; it is soluble in alkali-lye, and is precipitated unaltered on the addition of an acid. Vap. densities taken at 550°–600° indicated that dissociation had taken place; and **arsenic trisulphodiselenide,** $As_2S_3Se_2$, is produced in an analogous way from arsenic trisulphide and selenium. It forms thin, ruby-red plates. The vap. density at 750° shows that dissociation occurs. E. von Gerichten obtained **antimony disulphoselenide,** Sb_2S_2Se, in the wet way by precipitation with a soln. of selenium disulphide in potassium hydroxide. G. Hofacker obtained a reddish-brown powder of **antimony trisulphodiselenide,** $Sb_2S_3Se_2$, by treating with acid a soln. of sodium selenotrisulphantimonate. The chemical individuality of these substances has not been established for **lead bismuth sulphoselenides,** *vide supra*, bismuth selenide.

C. Messinger prepared **sodium sulphotriselenoarsenate,** $Na_3AsSSe_3.9H_2O$, together with selenotrisulphoarsenate when arsenic trisulphide is dissolved in a mixture of sodium sulphoselenide, and selenide: $As_2Se_3+Na_2Se_2S+3Na_2S=Na_2Se+Na_3AsS_3Se+Na_3AsSe_3S$; the selenotrisulphoarsenate is deposited first when the soln. is slowly cooled. The sulphotriselenoarsenate furnishes red hygroscopic prisms which are decomposed by acids with the evolution of hydrogen sulphide and selenide, and the precipitation of selenium and arsenic trisulphide. W. Muthmann and A. Clever obtained possibly a mixed salt, $Na_3AsS_{1\cdot5}Se_{2\cdot5}.9H_2O$, from a soln. of 5 grms. sodium hydroxide, 7·5 grms. of water, sodium sulphide, and 6 grms. of arsenic pentasulphide. They also obtained the corresponding **potassium sulphoselenoarsenate,** $K_3AsS_{1\cdot5}Se_{2\cdot5}.6H_2O$. C. Messinger reported **sodium diselenodisulphoarsenate,** $Na_3AsS_2Se_2.9H_2O$, to be formed by melting arsenic, sulphur, and selenium to form As_2SSe_4, and treating the product with a hot soln. of sodium hydrosulphide. Reddish-yellow, prismatic crystals separate on cooling. The compound is decomposed by acids. When this compound is boiled with the calculated quantity of sodium hydrosulphide, brownish-yellow prisms with the composition $Na_3AsS_{2\cdot5}Se_{1\cdot5}.8H_2O$, are formed; if arsenic disulphoselenide be similarly treated with sodium hydrosulphide, **sodium trisulphoselenoarsenate,** $Na_3AsS_3Se.8H_2O$, crystallizes at −7° in brownish-yellow prisms. The crystals are stable in dry air, and are decomposed by moist air and by acids. He also made $Na_3AsS_{3\cdot5}Se_{0\cdot5}.8H_2O$.

G. Hofacker obtained **sodium trisulphoselenoantimonate,** $Na_3SbS_3Se.9H_2O$, by adding alcohol to a soln. of a gram-atom of selenium in a mol of sodium sulphoantimonate. It is isomorphous with the corresponding seleno- and sulpho-salts. The yellow salt becomes brown in air; it loses all its water but no selenium, at 100°; acids precipitate antimony trisulphodiselenide. I. Pouget obtained some mixed salts, $Na_3SbS_{1\cdot5}Se_{1\cdot5}.9H_2O$; and $Na_3SbS_{1\cdot5}Se_{2\cdot5}.9H_2O$, from soln. of antimony and selenium in sodium selenide; and likewise **potassium sulphoselenoantimonite,** $K_{10}Sb_4S_5Se_6.4H_2O$, from a soln. of antimony, and selenium in potassium sulphide.

J. Meyer prepared **phosphorus disulphoselenide,** P_4S_2Se, by melting together the corresponding proportions of the constituent elements. It melts at 190°–200°; and closely resembles the selenide P_4Se_3. It may not be a true compound.

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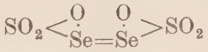
§ 17. Oxysulphoselenium Compounds

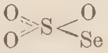
G. Magnus[1] observed that selenium rapidly dissolves in warm fuming sulphuric acid; but, added N. W. Fischer, no compound with sulphur trioxide is formed. G. Magnus said that selenium is precipitated as a red powder when water is added to the green soln., and only about one-fiftieth part of the selenium remains in soln., and it is precipitated by hydrogen sulphide. If the green soln. is warmed, selenium and sulphur dioxides are formed; and water precipitates only a little selenium from the soln. decolorized by boiling. G. Magnus explained these facts by assuming that selenium dissolves in the sulphuric acid without alteration, while N. W. Fischer said that the selenium is present in an oxidized state because sulphur dioxide is formed in the process of soln., and on adding water, the sulphurous and selenious acids react to form selenium and sulphuric acid. According to L. Gmelin, sulphuric acid containing the anhydrous acid dissolves selenium at ordinary temp., while ordinary sulphuric acid dissolves it when boiled for some time—the former gives a soln. precipitable by water and yields a filtrate which becomes faintly turbid when treated with hydrogen sulphide; while the latter gives a filtrate rich in selenious acid. Both soln. are dark green, and turn yellow when boiled, and then suddenly becomes colourless. The colourless soln. no longer gives a precipitate with water, since it contains selenious acid, but it yields an orange-yellow precipitate with hydrogen sulphide. R. Weber, and A. Hilger also studied the action of sulphuric acid on selenium. According to R. Auerbach, cryoscopic measurements show that metalloidal selenium dissolves in pyrosulphuric acid as Se_2, and that at 130°, the element becomes metallic when it is present in single atoms. At the same time the colour changes from green to yellow. By adding water to the soln. of Se_2 in pyrosulphuric acid, at 20°, the colour changes from green through yellow and red to violet, as the size of the particles increase, the metalloid is then precipitated; above 130°, the colour change is from yellow, through red, to blue, and the metallic form is precipitated. If the yellow, metallic soln. is coagulated at ordinary temp., Se_2-mols are first reformed, and the colour changes in the regular way until the metalloid is precipitated.

A. C. Schultz-Sellack found that when the dark green soln. of selenium in conc. sulphuric acid is heated in a sealed tube, it acquires the same pale yellow colour characteristic of a soln. of selenium in carbon disulphide examined in a thick layer. The selenium is not oxidized at a low temp. When the vapour of sulphur trioxide is passed over selenium at ordinary temp. it forms a mush which slowly yields a yellow powder of **selenium sulphotrioxide,** $SeSO_3$; the reaction is faster at a higher temp., and considerable amounts of selenium and sulphur dioxide are formed. Selenium sulphotrioxide was prepared by R. Weber. When powdered selenium is mixed with sulphur trioxide, the temp. rises, and a dark green liquid is formed. The green liquid crystallizes in about ten minutes, and it does not again liquefy when warmed. If the temp. of the reaction be 15°–17°, only a little sulphur dioxide is evolved, the excess of trioxide remains unchanged, and it can be separated from the dark green drops of the sulphotrioxide. E. Divers and M. Shimose obtained a green, unstable liquid, probably selenium sulphotrioxide, by the action of sulphur trioxide on selenium dichloride. F. W. O. de Coninck observed that a little of the sulphoxide is formed by the reversible action of sulphuric acid on red amorphous selenium: $Se+H_2SO_4 \rightleftharpoons SeSO_3+H_2O$. The compound was only prepared by W. Prandtl and P. Borinsky. S. Littmann noticed that the sulphotrioxide is formed during the conc. of seleniferous sulphuric acid. R. Weber emphasized the analogy between sulphur sesquioxide, S_2O_3, and selenium sulphotrioxide, $(SeS)O_3$. E. Divers and T. Shimidzu regarded selenium sulphotrioxide as a *selenium sulphite*, $Se(SO_3)$, constituted:



$$SO_2<\begin{matrix}O & & O\\ \vert & & \vert\\ Se & = & Se\end{matrix}>SO_2$$

because (i) the hydrolysis with water resolves it partly into sulphurous acid and partly into what is equivalent to a base: $Se_2(SO_3)_2+2H_2O=(Se+SeO_2)+2H_2SO_3$, and partly like silver sulphite into metal and sulphuric acid: $Se_2(SO_3)_2+2H_2O=2Se+2H_2SO_4$; hence, the sulphotrioxide stands in the same relation to the sulphites of strong metals as the corresponding chlorides do to the metal chlorides. (ii) They are not only formed by the direct union of their quasi-metal with sulphur trioxide, but they can be partially decomposed in vacuo into these components: $Se_2(SO_3)_2=2Se+(SO_3)_2$; (iii) it dissolves in fuming sulphuric acid without decomposition, and when thus dissolved, it is decomposed like a sulphite by hydrochloric acid: $Se_2(SO_3)_2+2HCl=H_2SO_3+Cl_2Se_2(SO_3)$—*vide supra*—and this reacts with hydrochloric acid, $Cl_2Se_2(SO_3)+HCl=Se_2Cl_2+HClSO_3$, as in the case of the corresponding chlorosulphite of mercury: $Cl_2Hg_2(SO_3)+H(OH)=Hg_2Cl_2+(HO)HSO_3$. R. Auerbach said that selenium dissolves in pyrosulphuric acid as Se-mols. W. Prandtl and P. Borinsky represented it, as in the case of sulphur sesquioxide (*q.v.*):



$$\begin{matrix}O\\O\end{matrix}>S<\begin{matrix}O\\Se\end{matrix}$$

Selenium sulphotrioxide was described by R. Weber as a dark green liquid which freezes to a dirty green mass consisting of microscopic, prismatic crystals. These crystals form a yellow powder. E. Divers and M. Shimose obtained what they regarded as a yellow, amorphous modification, by heating the sulphoxide *in vacuo* slowly and maintaining a moderate temp. for a long time. With more rapid heating, reddening occurs before the yellowing stage is completed, and the mass contains a much greater proportion of selenium than when the heat is better graduated. According to R. Weber, selenium sulphotrioxide is more stable than sulphur sesquioxide. The sulphotrioxide is not decomposed by gentle heat; and after it has been solidified, it cannot be melted without decomposition into sulphur, and the dioxides of sulphur and selenium. A. C. Schultz-Sellack said that when gently heated, it decomposes into selenium and sulphur trioxide. E. Divers and M. Shimose found that the sulphotrioxide very slowly becomes dissolved at ordinary temp. owing to decomposition; but it may be heated to 35° for some time without appreciable alteration. Decomposition begins to show itself at 40° by a change of the green colour to brown, and by the escape of sulphur dioxide, although this is exceedingly slow, even when 90° is reached. At 120° and upwards, however, sulphur dioxide is steadily evolved, the colour gradually changes to bright yellow, and the vol. slightly shrinks. On continuing the heating the colour changes to orange, and then reddens and darkens until it becomes identical with that of selenium. Selenium, in fact, is here formed together with its ordinary oxide. As indicated above, a prolonged heating in vacuo changes it into a yellow, amorphous modification. R. Weber said that the sulphotrioxide is decomposed by water, forming sulphuric acid, sulphur dioxide, selenium dioxide, and selenium. E. Divers and M. Shimose said that the yellow sulphotrioxide hisses when thrown into water, just like the green sulphoxide, and the tellurium sulphoxide, and it is therefore a sulphuric oxide compound; it bears a heat of 120°, and therefore its sulphur trioxide is in combination; it does not contain any green sulphoxide, by which the properties might be explained; and its yellow colour cannot be regarded as due to free selenium. The reactions with water are indicated above. A sulphuric acid soln. of selenium sulphotrioxide behaves like a sulphite when treated with hydrochloric acid, decomposing in two phases as indicated above. R. Weber found that selenium sulphotrioxide, like sulphur sesquioxide, is insoluble in sulphur trioxide, and it is dissolved by warm hydrated sulphur trioxide, forming an intense green soln., and if enough sulphur trioxide be present to solidify on cooling, the crystals of the sulphur trioxide are coloured green by the selenium sulphotrioxide; E. Divers and M. Shimose added that the sulphotrioxide can be oxidized by sulphur trioxide: $SeSO_3+SO_3=SeO_2+2SO_2$. R. Weber found that fuming sulphuric acid forms a green soln. with the sulphotrioxide, and the soln. behaves as if it were a soln. of selenium in fuming sulphuric acid; the green-coloured soln. can be kept without change, but when treated with water, most of the selenium separates out, and the soln. is decolorized by heat, forming sulphur and selenium dioxides. The sulphotrioxide dissolves in sulphuric acid, H_2SO_4, forming a green soln.; in 88 per cent. H_2SO_4, a brown soln.; and in 83 per cent. H_2SO_4, it forms a soln., which begins to decompose with the separation of selenium. R. Weber found that there is a vigorous reaction with ammonia, forming a brownish-red substance.

R. Weber[2] found that dry selenium dioxide readily unites with sulphur trioxide when the mixture is warmed in a sealed tube, forming the complex $SeO_2.SO_3$, a kind of selenium analogue of S_2O_5—**selenium sulphopentoxide,** $SeSO_5$, or *selenyl sulphate*, $(SeO)SO_4$. R. Metzner found that, at 50°, selenium dioxide dissolves copiously in sulphuric acid, sat. with sulphur trioxide; if, before saturation with selenium dioxide, the liquid is cooled, in a dry atm., crystals of the sulphopentoxide separate out; and these can be dried by press. between porous tiles. The compound readily fuses; and the liquid freezes to a crystalline mass; and R. Metzner added that with slow cooling, fine, acicular, deliquescent crystals are produced. These do not fume in air. The heat of formation is 4·3 Cals.

It might be anticipated that just as pyrosulphuric acid, $H_2S_2O_7$, or $H_2SO_4.SO_3$, is formed by the union of sulphur trioxide and sulphuric acid, so **selenatosulphuric acid,** H_2SSeO_7, would be formed by the union of sulphuric acid with selenium trioxide, $H_2SO_4.SeO_3$, or of selenic acid with sulphur trioxide, $H_2SeO.SO_3$. J. Meyer and V. Stateczny[3] found that sulphur trioxide is freely absorbed by selenic acid with the evolution of much heat. The f.p. curve of the mixture is shown in Fig. 66. Selenatosulphuric acid, H_2SeSO_7, is a colourless, fuming liquid which forms a solid melting at 6·6°. When strongly heated, it gives off oxygen, forming selenium dioxide and sulphuric acid; and if dil. with water, it forms a mixture of selenic and sulphuric acids. When a mixture of potassium hydroselenate and hydrosulphate is melted, water is given off, and **potassium selenatosulphate,** K_2SeSO_7, or $K_2[(SO_4)Se(O_3)]$, is formed. It is also obtained by the action of sulphur trioxide on potassium selenate in a sealed tube at 120°. The salt melts at 122°; it is freely soluble in water, but is at the same time decomposed into its constituents. A mixture of sulphur trioxide and ammonium selenate in a sealed tube at 100°, forms **ammonium selenatosulphate,** $(NH_4)_2SeSO_7$, which decomposes as it is melted; and it is also decomposed by moist air. A mixture of barium selenate and sulphur trioxide in a sealed tube at 200° furnishes **barium selenatosulphate,** $BaSeSO_7$. It decomposes when melted; and by exposure to air; with water it gives a precipitate of barium sulphate, and a soln. of selenic acid. The properties of **selenatodisulphuric acid,** $H_2S_2SeO_{10}$, or $H_2SeO_4.2SO_3$, or $H_2[(SO_4)_2Se(O_2)]$, are similar to those of selenatosulphuric acid; it melts at 20°.

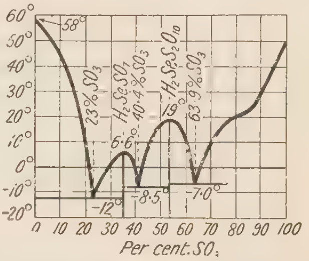


Fig. 66.—Freezing-point Curve of the System: H_2SeO_4–SO_3.

According to S. Cloez,[4] when selenium is treated with potassium sulphate in a sealed tube at 130°, **potassium monoselenothiosulphate,** K_2SeSO_3, is formed. B. Rathke obtained it by evaporating a soln. of selenium in aq. potassium sulphite—some selenotrithionate is formed at the same time. The sulphates of ammonium, sodium, and magnesium similarly furnish unstable selenothiosulphates. B. Rathke was unable to make *potassium selenoselenate,* $K_2Se_2O_3$. P. Rehländer prepared **rubidium selenothiosulphate** by dissolving selenium in a soln. of rubidium sulphite, and recovering the solid by precipitation or evaporation; similarly with **cæsium selenothiosulphate.** F. von Schaffgotsch said that selenium dissolves freely in a soln. of sodium sulphite; H. Uelsmann, in one of ammonium sulphite; and B. Rathke added that a soln. of 365 parts of potassium sulphite dissolves 102 parts of selenium; and 360 of magnesium sulphite, 116 parts of selenium; while a soln. of barium sulphite has no solvent action. F. Förster and co-workers observed the possible formation of this salt in the decomposition of sulphurous acid (*q.v.*) in the presence of selenium or selenious acid. B. Rathke found that the selenothiosulphates are isomorphous with the thiosulphates. The potassium salt turns brown when heated, forming a polysulphide; it is partially decomposed by water, with the separation of selenium, and the ultimate formation of selenatothiosulphate. The soln. is decomposed by iodine with the ultimate oxidation of the precipitated selenium; acids precipitate all the selenium; sulphur dioxide behaves similarly; a neutral soln. of silver nitrate precipitates part of the selenium, while an ammoniacal soln. reacts: $K_2SSeO_3+Ag_2O=Ag_2Se+K_2SO_4$; a soln. of barium chloride, or baryta-water, precipitates selenium and barium sulphite; similarly also with calcium and manganous salts; neutral cadmium salts precipitate **cadmium selenatothiosulphate,** and when the soln. is boiled, selenium selenide and sulphuric acid are formed; mercuric cyanide reacts, $K_2SSeO_3+HgCy_2+H_2O=HgSe+K_2SO_4+2HCy$; ferric chloride precipitates selenium and ferric oxide. *Confer* F. Förster, polythionic acids.

C. A. Cameron and J. Macallan observed no sign of the formation of *selenodithionic acid,* $H_2Se_2O_6$, when selenium dioxide is dissolved in selenic acid; but F. Förster and co-workers observed its possible formation in the decomposition of sulphurous acid (*q.v.*) in the presence of selenium or selenious acid.

According to H. O. Schulze,[5] when selenious and sulphurous acids react in aq. soln., selenium is precipitated when the molar proportion, $H_2SO_3 : H_2SeO_3 = 2 : 1$; if the proportion deviates from the 2 : 1-ratio a mixture of **monoselenotetrathionic acid,** $H_2SeS_3O_6$, and of **diselenotrithionic acid,** $H_2Se_2SO_6$, is formed—the former if the sulphurous acid is in excess: $3SO_2+2H_2O+SeO_2=H_2SO_4+H_2S_2SeO_6$; and the latter, if the selenious acid is in excess: $2SO_2+2SeO_2+2H_2O=H_2SO_4+H_2SSe_2O_6$. The mixture with the excess of sulphurous acid can be boiled without change, but with selenious acid in excess, selenium separates; both acids are decomposed by hydrochloric acid with the separation of selenium; and hence H. Rose emphasized the need for the presence of an excess of this acid when precipitating selenium by sulphuric acid. E. Divers and T. Shimidzu said that a selenothionic acid is formed when hydrogen selenide in excess is passed into sulphurous acid. The free acids are known only in soln. G. T. Morgan and H. D. K. Drew showed that selenium acetylacetone reacts quantitatively with sodium or potassium hydrosulphite, producing the corresponding alkali monoselenotrithionate: $(C_5H_6O_2:Se)_2+4NaHSO_3=2C_5H_8O_2+2Se(NaSO_3)_2$. G. T. Morgan and co-workers found that with sulphurous acid, monoselenotrithionic acid is formed: $(C_5H_6O_2:Se)_2+4H_2SO_3=2C_5H_8O_2+2Se(HSO_3)_2$. The acid could not be obtained in conc. soln. because, when its aq. soln. is evaporated at the ordinary temp. under reduced press., red selenium separates when a conc. of approximately 50 per cent. (or $8N$-) is reached. At higher conc., the aq. soln. deposits selenium and evolves sulphur dioxide, even at 0°. On treatment with aq. thallous hydroxide, selenodithionic acid yields thallous selenide and sulphuric acid: $Se(SO_3H)_2+2TlOH=Tl_2Se+2H_2SO_4$.

H. O. Schulze observed that the aq. soln. of the free monoselenotrithionic acid is stable in darkness, but it is slowly decomposed in light with the precipitation of selenium, and the evolution of sulphur dioxide. When evaporated on the water-bath, a crust of iron-grey selenium forms. A small proportion of selenium does not change the soln., but with a large proportion, or with the application of heat, selenium and sulphur dioxide are formed: $H_2SeS_2O_6=H_2SO_4+SO_2+Se$; sulphuric acid decomposes the acid only when hot, or when conc. soln. are used; the acid cannot be neutralized by potassium hydroxide, ammonia, or baryta-water without decomposition; and barium chloride precipitates barium sulphate by the decomposition of the acid: $BaS_2SeO_6=BaSO_4+SO_2+Se$. The mode of formation, the reactions of the acid, and the analysis of the barium salt are in agreement with the formula assigned to this acid. B. Rathke said that the free acid behaves like trithionic acid excepting that a mixture of selenium and sulphur is precipitated instead of sulphur alone. G. T. Morgan and J. D. M. Smith found that the monoselenotrithionates give a red precipitate on boiling with hydrogen dioxide; they do not react with even boiling soln. of $4N$-H_2SO_4, or more dil. acid; red selenium separates when boiled with $2N$-HCl, or $2N$-HNO_3; hydrogen sulphide gives a yellow precipitate which becomes orange-red on boiling; sodium hyposulphite gives a precipitate of red selenium in the cold; silver nitrate gives a brownish-black precipitate; mercurous nitrate, a greenish-black precipitate; mercuric chloride, a yellow precipitate, becoming orange, then buff, and then black on boiling; stannous chloride, slowly milky, then a pale yellow precipitate is formed, becoming orange-yellow and then orange-red on boiling; and potassium permanganate with $2N$-H_2SO_4 is first decolorized, it then turns yellow, then green, and finally forms a bronze-green precipitate.

According to H. O. Schulze, **ammonium monoselenotrithionate,** $(NH_4)_2S_2SeO_6$, is known only in aq. soln., and it is formed by neutralizing a soln. of the acid with ammonia. G. T. Morgan and J. D. M. Smith obtained it by double decomposition with selenium acetylacetone and ammonium hydrosulphite. It is somewhat unstable, and separated as a mass of colourless needles, which rapidly reddened on exposure to air. If a soln. of the salt be reprecipitated with alcohol-ether, the colourless needles soon acquired a fawn colour. G. T. Morgan and J. D. M. Smith prepared **lithium selenotrithionate,** $Se(LiSO_3)_2.3H_2O$, by shaking a mixture of 7 grms. of finely divided selenium acetylacetone and 5 grms. of dihydrated lithium sulphite with 45 c.c. of $2N$-H_2SO_3 for an hour; extracting with ether to remove acetylacetone; precipitating unchanged lithium sulphite by adding absolute alcohol; and concentrating the filtrate under reduced press. The red selenium simultaneously precipitated is removed by filtration through a layer of French chalk, and the liquid evaporated over sulphuric acid in vacuo. The colourless, hexagonal plates rapidly deliquesce in air; and then decompose with the separation of selenium. The salt is very soluble in water. A mixture of 7 grms. of selenium acetylacetone, 9 grms. of sodium hydrosulphite, and 30 c.c. of water furnishes colourless crystals of **sodium selenotrithionate,** $NaSeS_2O_6.4H_2O$, which can be purified by dissolving in cold water, and precipitating from the filtered soln. by the addition of alcohol. The colourless, prismatic needles are freely soluble in cold water, and readily form supersaturated soln. The salt readily effloresces in a dry atm., forming the anhydrous salt. The same salt was made by G. T. Morgan and H. D. K. Drew.

According to B. Rathke, **potassium monoselenotrithionate,** $K_2S_2SeO_6$, is formed, along with some potassium selenothiosulphate and thiosulphate, when selenium is dissolved in an aq. soln. of potassium sulphite; when a soln. of potassium selenothiosulphate and hydrosulphate is evaporated; by dissolving selenium in a soln. of potassium sulphite mixed with a little hydrosulphite, or in hydrosulphite alone at 60°–70°; and by adding selenious acid to a soln. of potassium selenothiosulphate mixed with an excess of potassium sulphite—the warm liquid deposits needle-like crystals of the salt on cooling, and when they are washed with cold water, the salt is obtained in a fair degree of purity. B. Rathke represented the reaction: $2K_2SeSO_3=K_2SeS_2O_6+K_2Se$; and $2K_2Se+3SeO_2=2K_2SeO_3+3Se$; and H. Schulze: $3SO_2+SeO_2+2H_2O=H_2SO_4+H_2S_2SeO_6$. O. Heuer prepared the salt by the action of selenious acid on potassium sulphite, $3K_2SO_3+SeO_2=K_2SeS_2O_6+K_2SO_4+K_2O$, and $3K_2SO_3+2SeO_2=K_2SeS_2O_6+K_2SO_4+K_2SeO_3$. When selenious acid acts on potassium thiosulphate, both potassium trithionate and selenotrithionate are formed: $SeO_2+4K_2S_2O_3=K_2S_4O_6+K_2SeS_4O_6+2K_2O$; followed by $K_2SeS_4O_6+6KOH=3K_2S_2O_3+2K_2SO_3+2Se+3H_2O$; and $K_2S_4O_6+K_2SO_3=K_2S_3O_6+K_2SeO_3$, as well as: $3K_2SO_3+SeO_2+H_2O=K_2SeS_2O_6+K_2SO_4+2KOH$. It is not possible to obtain this salt by neutralizing the free acid with bases since on evaporation the salt is all decomposed; but G. T. Morgan and co-workers obtained it by neutralizing a $2N$-soln. of monoselenotrithionic acid with a soln. of the alkali hydroxide, and precipitating with alcohol; and also from selenium acetylacetone and potassium hydrosulphite, as indicated above. The precipitate is extracted with ether to remove acetylacetone, and the aq. layer mixed with alcohol to complete the deposition of the selenotrithionate. G. T. Morgan and H. D. K. Drew said that the potassium salt, $Se(KSO_3)_2$, appeared in colourless, lustrous scales or plates when rapidly crystallized from aq. soln., and in long, transparent, silky needles when slowly formed. It is the least soluble of all the alkali monoselenotrithionates. O. Heuer found that when the dry salt is heated decomposition sets in at about 115°, forming selenium, sulphur dioxide, and sulphate: $K_2SeS_2O_6=Se+SO_2+K_2SO_4$. The clear aq. soln. of potassium selenotrithionate was found by B. Rathke to decompose on standing partly to selenium and potassium dithionate, and partly to selenium potassium sulphate, and sulphurous acid, the latter is favoured by boiling the soln., or by evaporating it over conc. sulphuric acid. O. Heuer represented the reaction: $K_2SeS_2O_6=K_2SO_4+SO_2+Se$. With a soln. of the barium salt, B. Rathke observed that barium sulphate is precipitated; and on evaporation over a water-bath, the salt decomposes: $BaS_2SeO_6=BaSO_4+SO_2+Se$. A soln. of the potassium salt gives no precipitate when treated in the cold with acids, but boiling soln. give a precipitate of selenium and sulphur. These reactions agree with those observed by H. O. Schulze with the free acid. Sulphur dioxide has no perceptible action; and barium chloride gives no precipitate; whilst the reactions with hydrochloric acid, potassium hydroxide, and baryta-water resemble those of the free acid. A soln. of the barium salt with bromine-water gives a precipitate of barium sulphate. O. Heuer observed that in the presence of iodine, potassium selenotrithionate decomposes: $K_2SeS_2O_6$

$+2H_2O+I_2=K_2SO_4+H_2SO_4+Se+2HI$; and with hydrogen sulphide, it reacts: $K_2SeS_2O_6+3H_2S=K_2S_2O_3+Se+3S+3H_2O$. The reaction with copper sulphate is represented by: $K_2SeS_2O_6+CuSO_4+2H_2O=CuSe+K_2SO_4+2H_2SO_4$. H. O. Schulze found that an ammoniacal soln. of a silver salt reacts: $K_2S_2SeO_6+Ag_2O+2NH_3+H_2O=K_2SO_4+Ag_2Se+(NH_4)_2SO_4$, and similarly with the barium salt—*vide supra* for some general reactions. According to O. Heuer, potassium selenotrithionate behaves towards metal salts as if a selenothiosulphate were first formed, and then decomposed either (*a*) into selenide and sulphate, or (*b*) into selenium, sulphur dioxide, and sulphate. The action of copper, silver, and mercuric salts illustrates the first action. In the case of mercuric chloride the reaction is represented: $2K_2SeS_2O_6+3HgCl_2+4H_2O=Hg_3Se_2Cl_2+4H_2SO_4+4KCl$, and this is supposed to be the resultant of $K_2SeS_2O_6+HgCl_2=HgSeS_2O_6+2KCl$, followed by $HgSeS_2O_6+2H_2O=HgSe+2H_2SO_4$, and by $2HgSe+HgCl_2=Hg_3Se_2Cl_2$. In the case of cadmium sulphate, lead acetate, and ferrous chloride the reactions are symbolized: $RSeSO_3+H_2SO_4=H_2SO_3+Se+RSO_4$. *Confer* F. Förster, polythionic acids.

G. T. Morgan and J. D. M. Smith prepared **rubidium selenotrithionate,** $Se(SO_3Rb)_2$, by shaking, as in the case of the sodium salt, a mixture of 1·8 grms. of selenium acetylacetone, 3·6 grms. of rubidium hydrosulphite, and 10 c.c. of water. The small, colourless crystals are dissolved in cold water and precipitated by alcohol. The well-defined, colourless prisms are more soluble in water than the potassium salt, and less soluble than the sodium and cæsium salts. Similarly, **cæsium selenotrithionate,** $Se(SO_3Cs)_2$, can be prepared. It crystallizes from hot, dil. alcohol in colourless needles, and from water, in transparent, tabular prisms.

H. O. Schulze observed that if the acid be neutralized with freshly precipitated, well-washed barium carbonate, a mixture of barium sulphate and carbonate coloured by selenium is precipitated, and the pale yellow, neutral filtrate is a soln. of **barium monoselenotrithionate,** $BaSeS_2O_6$, free from other salts. G. T. Morgan and J. D. M. Smith obtained the *dihydrate*, $BaSe(SO_3)_2.2H_2O$, from 9 grms. of barium sulphate, 7 grms. of selenium acetylacetone, and 20 c.c. of $3·3N$-H_2SO_3. The heavy, colourless, crystalline mass can be purified by dissolving in water and precipitating with alcohol. The colourless needles redden on exposure to air. The corresponding **calcium selenotrithionate** is so soluble in water and alcohol that it was not precipitated by ether from these soln. For **mercuric selenotrithionate,** $HgSeS_2O_6$, *vide supra*.

H. O. Schulze obtained an aq. soln. of **diselenotrithionic acid,** $H_2Se_2SO_6$, as indicated above; and it is rather less stable than is the case with monoselenotrithionic acid. The aq. soln. of the acid is decomposed by boiling or by exposure to light; and to a far less degree when kept in the dark. As in the case of monoselenotrithionic acid, the diselenotrithionic acid is decomposed by acids and alkalies, but it can be neutralized by barium carbonate without any marked decomposition. The preparation of the barium salt is more difficult than is the case with the monoselenotrithionic acid because the excess of selenious acid is not completely abstracted by barium carbonate. The soln. of the barium salt slowly decomposes in darkness, and when boiled or evaporated deposits selenium and barium sulphate; it is also decomposed by hydrochloric acid; an ammoniacal soln. of a silver salt gives a black precipitate of barium sulphate and silver selenide, and the filtrate gives a precipitate—probably of barium selenate—when treated with barium chloride.

J. F. Norris and H. Fay[6] showed that the reaction between selenium dioxide and sodium thiosulphate probably occurs: $SeO_2+4Na_2S_2O_3=2Na_2S_4O_6+Se+2Na_2O$, in conc. soln., selenium is precipitated, and the soln. becomes alkaline; but in dil. soln., no selenium is precipitated, and the reaction is not complete according to this equation owing to the sodium hydroxide formed neutralizing part of the selenious acid which does not therefore enter into reaction. In the presence of hydrochloric acid, the reaction which occurs is $SeO_2+4Na_2S_2O_3+4HCl$

$=Na_2S_4SeO_6+Na_2S_4O_6+4NaCl+2H_2O$. No selenium is precipitated, but **sodium monoselenopentathionate,** $Na_2S_4SeO_6$, is formed which, although it cannot be isolated, gives the characteristic tests for pentathionates, with the difference that selenium, not sulphur, is precipitated; a dil. soln. of the salt can be boiled without change, but stannous chloride precipitates selenium in a few minutes; sodium thiosulphate effects the same result, but more slowly. The sodium tetrathionate, formed according to the equation, was isolated and identified. No other salt has been prepared. O. Heuer's theory of the reaction between selenious acid and potassium thiosulphate is indicated above. He showed that potassium tetrathionate and selenopentathionate are formed, and that with the aid of alcohol in the cold it is possible to isolate these two salts; and the reaction can be expressed: $3SeO_2+4K_2S_2O_3=K_2S_4O_6+K_2SeS_4O_6+2K_2SeO_3$; followed by $2K_2SeS_4O_6+6KOH=3K_2S_2O_3+2K_2SO_3+2Se+3H_2O$; by $K_2S_4O_6+K_2SO_3=K_2S_3O_6+K_2S_2O_3$; and by $K_2S_3O_6+Se=K_2S_3SeO_6$. Potassium tetrathionate as well as **potassium selenotetrathionate,** $K_2SeS_3O_6$, is precipitated when a conc. soln. of selenious acid is mixed with a conc. soln. of potassium thiosulphate.

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§ 18. Selenatosulphates and Sulphatoselenates

E. von Gerichten[1] prepared a series of **selenatosulphates,** and a series of **sulphatoselenates,** but there is little to distinguish one from the other; and no proof has been given that both series are not solid soln. or isomorphous mixed crystals. The salts are isomorphous with the corresponding selenates and sulphates. By mixing conc. soln. of potassium selenate and copper sulphate, **potassium copper selenatosulphate,** $K_2SeO_4.CuSO_4.6H_2O$, is formed; if the soln. of copper sulphate is acidified, part of the potassium selenate may be replaced by the sulphate. Similarly, **potassium copper sulphatoselenate,** $K_2SO_4.CuSeO_4.6H_2O$, was formed in light blue, monoclinic crystals. The potassium sulphate may be in part replaced by selenate. Similarly with **potassium magnesium selenatosulphate,** $K_2SeO_4.MgSO_4.6H_2O$, and

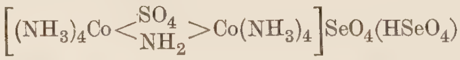
potassium magnesium sulphatoselenate, $K_2SO_4.MgSeO_4.6H_2O$; with **potassium zinc selenatosulphate,** $K_2SeO_4.ZnSO_4.6H_2O$, and **potassium zinc sulphatoselenate,** $K_2SO_4.ZnSeO_4.6H_2O$; with **potassium cadmium selenatosulphate,** $K_2SeO_4.CdSO_4.6H_2O$, and **potassium cadmium sulphatoselenate,** $K_2SO_4.CdSeO_4.6H_2O$; with **potassium manganese selenatosulphate,** $K_2SeO_4.MnSO_4.6H_2O$, and **potassium manganese sulphatoselenate,** $K_2SO_4.MnSeO_4.6H_2O$; with **potassium ferrous selenatosulphate,** $K_2SeO_4.FeSO_4.6H_2O$, and **potassium ferrous sulphatoselenate,** $K_2SO_4.FeSeO_4.6H_2O$; with **potassium cobaltous selenatosulphate,** $K_2SeO_4.CoSO_4.6H_2O$, and **potassium cobaltous sulphatoselenate,** $K_2SO_4.CoSeO_4.6H_2O$; and with **potassium nickel selenatosulphate,** $K_2SeO_4.NiSO_4.6H_2O$, and **potassium nickel sulphatoselenate,** $K_2SO_4.NiSeO_4.6H_2O$.

E. von Gerichten prepared **potassium aluminium selenatosulphate,** $K_2SeO_4.Al_2(SO_4)_3.24H_2O$, in octahedral crystals from a soln. of the component salts ; and likewise also with **potassium aluminium sulphatoselenate,** $K_2SO_4.Al_2(SeO_4)_3.24H_2O$. O. Pettersson found that with a soln. of equimolar parts of potash selenium alum, and potash-alum, crystals containing respectively 31·33 and 23·32 per cent. of SO_3 were obtained ; and with soln. containing 3 mols of potash selenium alum, and one mol of potash-alum, crystals containing respectively 13·48, 11·42, and 9·49 per cent. of SO_3 were obtained. The corresponding sp. gr. are :

SO_3 . .	31·33	23·82	13·48	11·42	9·49 per cent.
Sp. gr. .	1·77 (15·0°)	1·825 (14·2°)	1·900 (16°)	1·910 (17·6°)	1·921 (138°)

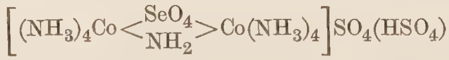
This shows that the magnitude of the mol. vol. rises and falls with the greater or less proportion of selenic acid in the compound. E. von Gerichten similarly prepared **potassium chromium selenatosulphate,** $K_2SeO_4.Cr_2(SO_4)_3.24H_2O$, and **potassium chromium sulphatoselenate,** $K_2SO_4.Cr_2(SeO_4)_3.24H_2O$; **potassium manganic selenatosulphate,** $K_2SeO_4.Mn_2(SO_4)_3.24H_2O$, and **potassium manganic sulphatoselenate,** $K_2SO_4.Mn_2(SeO_4)_3.24H_2O$; and **potassium ferric selenatosulphate,** $K_2SO_4.Fe_2(SO_4)_3.24H_2O$, and **potassium ferric sulphatoselenate,** $K_2SO_4.Fe_2(SeO_4)_3.24H_2O$.

J. Meyer and K. Gröhler prepared **cobaltic aquoselenatotetramminosulphate,** $[Co(NH_3)_4(H_2O)(SeO_4)]_2SO_4.4H_2O$; and **cobaltic aquosulphatotetramminoselenate,** $[Co(NH_3)_4(H_2O)(SO_4)]_2SeO_4.4H_2O$. J. Meyer and co-workers also prepared **cobaltic μ-amidosulphatoctamminohydroselenate,**



$$\left[(NH_3)_4Co{<}{}^{SO_4}_{NH_2}{>}Co(NH_3)_4\right]SeO_4(HSeO_4)$$

and **cobaltic μ-amidoselenatotetramminohydrosulphate**



$$\left[(NH_3)_4Co{<}{}^{SeO_4}_{NH_2}{>}Co(NH_3)_4\right]SO_4(HSO_4)$$

K. Hradecky[2] prepared **ammonium palladous sulphatoselenate**—*vide supra*, palladous selenate.

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§ 19. Selenophosphites and Selenophosphates

The *selenium phosphides* have been discussed in connection with the *phosphorus selenides*. Selenium can take the place of sulphur in the thiophosphates, forming a series of *selenophosphates*. O. Hahn[1] prepared **potassium selenophosphide** K—P=Se, by heating a mixture of equimolar parts of phosphorus selenide and potassium selenide, while protected from moisture, and in a current of hydrogen.

The red mixture becomes nearly white; if heated too strongly, the compound is decomposed. If it be not cooled in hydrogen, it will inflame in air. If a higher proportion of potassium selenide be employed, the excess remains uncombined. T. E. Thorpe and A. E. H. Tutton prepared phosphorus sulphoxide, $P_4S_4O_6$, by the action of sulphur on phosphorous oxide, and added that selenium appears to form a crystalline compound with phosphorous oxide, possibly **phosphorus selenoxide,** similar to the sulphoxide, but owing to the fact that the phosphorous oxide is largely decomposed at the temp. of the reaction, the sublimed substance is mixed with the products of the decomposition.

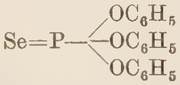
W. Muthmann and A. Clever obtained **potassium hydroselenophosphite,** $K_2HPSe_3.2\frac{1}{2}H_2O$, by the action of potassium hydroxide on phosphorus pentaselenide; or better, by gradually adding powdered phosphorus triselenide to a cold conc. soln. of potassium hydroxide, cautiously warming the mixture at 75°–78° until soln. takes place, and allowing the filtered liquid to crystallize in a freezing mixture; if the mixture is heated above 80°, complete decomposition takes place and hydrogen selenide is evolved. The selenophosphite crystallizes in highly lustrous octahedra-like forms, which do not, however, belong to the regular system as they show double refraction; it gradually decomposes in moist air with separation of selenium and hydrogen selenide: when heated, it gives off water vapour and hydrogen selenide, while selenium, and then selenium dioxide, sublime, leaving a residue of phosphate. It is sparingly soluble in cold water, easily so in hot water, and can be recrystallized from a conc. soln. of potassium hydroxide. The aq. soln. is neutral and pale yellow. With dil. acids, it yields hydrogen selenide, and selenium is gradually precipitated. Lead and silver salts give brownish, amorphous precipitates which gradually darken, and the supernatant soln. then contains phosphoric acid. Barium salts give a yellow, amorphous precipitate which quickly turns red. O. Hahn obtained **potassium selenodiphosphite,** $2K_2Se.P_2Se_3$, or $K_4P_2Se_5$, by heating a mixture of 2 mols of potassium selenide and a mol of phosphorus triselenide; and W. Muthmann and A. Clever prepared **potassium triselenodithiophosphite,** $2K_2S.P_2Se_3.5H_2O$, or $K_4PSe_3S_2.5H_2O$, by the action of potassium sulphide on the triselenide; it forms small, colourless, doubly-refractive crystals having an octahedral habit and an adamantine lustre, and is decomposed at about 80° with evolution of hydrogen sulphide and selenide. The aq. soln. is colourless, and when treated with acids yields hydrogen sulphide and selenide, whilst a reddish-brown compound mixed with sulphur is precipitated. When treated with salts of the heavy metals, it yields dark, amorphous precipitates. These compounds give well-crystallized products with an ammoniacal soln. of a magnesium salt.

F. Ephraim and E. Majler said that the **selenophosphates** of the alkali and alkaline earth metals, and magnesium can be prepared by the action of phosphorus pentaselenide on aq. soln. of the respective metals: $3R_2Se+P_2Se_5=2R_3PSe_4$; but in no case could the solid tetraselenophosphate be isolated because it is immediately decomposed by water: $R_3PSe_4+H_2O=H_2Se+R_3POSe_3$; the decomposition in some cases may proceed further, forming di- or tri-oxyselenophosphates; and intermediate products may be obtained as isomorphous mixtures of different oxyselenophosphates—*e.g.* greenish-yellow octahedra with the composition $K_3PSe_{2.5}O_{1.5}.H_2O$, were obtained from a sat. soln. of potassium hydroselenide and phosphorus pentaselenide. The compounds crystallized from a soln. rich in hydrogen selenide contain a larger proportion of selenium than when precipitated by alcohol. The oxyselenophosphates can be obtained from the metal hydroxide, and phosphorus pentaselenide; but, even in the presence of an excess of alkali, the normal salts sometimes hydrolyze with the formation of the monohydro-salts, as conditioned by the relative solubilities of the two salts in the mother-liquor. When dissolved in water, particularly hot water, all the compounds are hydrolyzed: $R_3PSe_4+4H_2O=R_3PO+4H_2Se$. The mother-liquors quickly oxidize on exposure to air, becoming red, and depositing selenium. The solid salts are fairly stable in dry air. Normal salts were obtained with the alkali metals; the alkaline earth metals furnish monohydro-salts.

W. Muthmann and A. Clever obtained **sodium oxytriselenophosphate,** $Na_3PSe_3O.10H_2O$, by the action of phosphorus triselenide on sodium hydroxide. It crystallizes from a conc soln. of sodium hydroxide in pale green, doubly-refracting prisms. The aq. soln. quickly decomposes; with acids, it yields hydrogen selenide and a brown precipitate containing selenium. When heated in a tube, it yields a sublimate of selenium, and a phosphate. It gives a well-crystallized compound with ammoniacal magnesia mixture. F. Ephraim and E. Majler prepared **ammonium oxytriselenophosphate,** $(NH_4)_3PSe_3O.10H_2O$, in leaflets, from a warm soln. of phosphorus pentaselenide and a sat. soln. of hydrogen selenide in conc. ammonia. The cold mother-liquor deposits octahedra and four-sided leaflets of $(NH_4)_5H(PSe_5O)_2.18H_2O$. Similarly there was obtained greenish-yellow, octahedral crystals of **potassium oxytriselenophosphate** in isomorphous association with a lower selenophosphate because the ultimate composition was $K_3PSe_{2\cdot5}O_{1\cdot5}.H_2O$. For the corresponding calcium salt, *vide infra.*

F. Ephraim and E. Majler prepared **barium hydrodioxydiselenophosphate,** $BaHPSe_2O_2.14H_2O$, as a microcrystalline powder, by treating phosphorus pentaselenide either with a soln. of barium hydroxide, or with a sat. soln. of hydrogen selenide in baryta-water. When 2 grms. of strontium hydroxide in aq. soln. are treated with 3 grms. of phosphorus pentaselenide, and the filtrate from the deposited selenium treated with alcohol, a light yellow precipitate is formed of **strontium hydrodioxydiselenophosphate** in isomorphous association with the trioxyselenophosphate, since the composition is $SrHPSe_{2/3}O_{1/13}.7H_2O$; with a larger excess of the pentaselenide, the colourless crystals have the composition $SrHPSe_{4/3}O_{8/3}.8H_2O$, which may be $2SrHPSeO_3+SrHPSe_2O_2+24H_2O$. With calcium hydroxide, and the smaller proportion of phosphorus pentaselenide, there is formed **calcium hydrodioxydiselenophosphate** in an amorphous association with **calcium hydrotrioxyselenophosphate,** $CaHPSeO_3.8H_2O$, which is produced when the larger proportion of phosphorus pentaselenide is used. An impure **magnesium hydrodioxydiselenophosphate** was also prepared by F. Ephraim and E. Majler.

F. Ephraim and E. Majler prepared **sodium trioxyselenophosphate,** $Na_3PSeO_3.20H_2O$, by digesting a conc. soln. of sodium hydroxide with phosphorus pentaselenide. The same substance was obtained when sodium hydroselenide was used in the place of sodium hydroxide. It crystallizes in needles. C. Grossmann prepared a number of derivatives of this acid—*e.g.* phenyl trioxyselenophosphate:



$$Se{=}P{-}\!\!\begin{cases}OC_6H_5\\OC_6H_5\\OC_6H_5\end{cases}$$

R. F. Weinland and G. Barttlingck prepared **potassium pentaselenatodiphosphate,** $3\cdot5K_2O.5SeO_3.P_2O_5.5\cdot5H_2O$, from a soln. of selenic acid, phosphoric acid, and potassium hydroxide in the molar proportions 1 : 4 : 1. The rod-like crystals are stable in air and do not effloresce over sulphuric acid. They are freely soluble in water. If the soln. has the above components in the proportion 1 : 2 : 2, colourless plates of **potassium selenatophosphate,** $2K_2O.2SeO_3.P_2O_5.3H_2O$, are formed. They do not effloresce over sulphuric acid. Likewise also with **rubidium selenatophosphate,** $2Rb_2O.2SeO_3.P_2O_5.3H_2O$; and **ammonium selenatophosphate,** $2(NH_4)_2O.2SeO_3.P_2O_5.3H_2O$.

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